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IN ENGLISH TRANSLATION

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Just published in complete translation from Russian,

THE GEOLOGY OF URANIUM

TODAY, WORLDWIDE INTEREST in fissionable material has focused more attention than ever on uranium—*the origin of its deposits, its mineralogy, and methods of investigation.* As a result, the Soviet *Journal of Atomic Energy* devoted an entire supplement (No. 6) to current problems on the geology of uranium, which was published December, 1957 in Russian.

Now this collection of twelve important papers by leading Soviet specialists is available, in English, for those Western scientists who must keep abreast of the latest developments in the field by their Russian counterparts. Here, in well written and concise style, are graphic expositions of the main problems encountered in current investigations, with attention directed mainly toward *the study of uranium deposits which formed contemporaneously with sedimentary rocks.* The important role of *diagenesis* and of subsequent *epigenetic and metamorphic* phenomena, which have produced redistribution and concentration of uranium under favorable geological conditions, is clearly illustrated by actual occurrences; processes which lead to formation of epigenetic infiltration uranium deposits in coal basins are keenly analyzed; and various hypotheses, reported in Soviet and foreign literature, on the origin of such deposits are discussed in detail.

Additionally, this new work covers *a comprehensive survey of aerial geophysical methods* in various countries; *methods for radiometric study of uranium in three-component ore containing radioactive elements of the uranium and thorium series;* a description of several *new* minerals (including recent data on *nenadkevite,* described earlier in the journal *Atomic Energy*); and the results of *thermal investigations* conducted on a number of uranium minerals, which, on the whole, open the door to the possibility of determining other minerals difficult to analyze. In short, this richly-authoritative volume not only reveals the most up-to-date Soviet progress, but also adds *new* knowledge to our growing storehouse of information and stimulates incentive for further investigation into THE GEOLOGY OF URANIUM.

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A COMPARATIVE STUDY OF THE SPATIAL DISTRIBUTION OF ELEMENTS IN A D.C. ARC AND IN AN IMPULSE ARC BY MEANS OF RADIOACTIVE ISOTOPES

Yu. I. Belyaev, E. E. Vainshtein, and V. V. Korolev

The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry
Acad. Sci. USSR, Moscow

It was demonstrated recently [1] that the use of an impulse arc operating according to the scheme suggested by Levintov [2], makes it possible to increase the accuracy and reproducibility of the spectrographic analysis of silicates appreciably. In the course of this work a number of factors were observed which can be interpreted as indicating a distribution of the elements in the interelectrode space which differs essentially from the one observed in the normal d.c. arc. In order to study this observation experimentally, use was made of a method suggested in our laboratory [3] for studying the spatial distribution of elements in the plasma of various sources by means of radioactive isotopes. Radioactive isotopes have also been used [4,5] for studying the process of evaporation of various elements in an impulse arc and in a d.c. arc.

The experimental technique used has been described in the papers cited [3, 4]. The curves (Figs. 1 and 2) give an idea of the nature of the distribution of a number of elements in the interelectrode gap of a d.c. arc, and of an impulse arc. As is evident from the diagrams independently of the shape of the distribution curves of the elements in the plasma of the d.c. arc, for the majority of the elements in the impulse arc, there is observed an uniform distribution with a clearly defined maximum located in the middle of the interelectrode gap. The only exceptions are tha alkali metals with low ionization potential values. The spatial distribution of these elements in the different souces differs insignificantly. It should be pointed out that the curves for the spatial distribution of potassium* during its evaporation in both souces, from carbonate and sulfate, differ from each other. In the latter instance, in the middle region of the interelectrode gap there is observed a clearly defined minium, the incidence of which, presumably, is the reason for the weakening ofthe lines of a number of the alkaline metals on addition of relatively large amounts of sodium sulfate to the test material,a phenomenon which has been noted previously in the literature [6,7]. The levelling of the distribution curve for the atoms of the alkali elements in the plasma of an impulse arc, is favored by dilution of the salts of these elements by a buffer mixture consisting of carbon powder and cupric oxide. Thus, in the mixture consisting of these components in the proportion of 1:1:2, the distribution curve for sodium in an impulse arc acquires the shape shown in Fig. 3. In this case, as is evident, the character of the distribution of the alkali elements in the interelectrode, is already almost indistinguishable from the distribution characteristic for such elements as zinc and copper.

In order to get a clearer picture of the character of the distribution of elements in an impulse arc, and in order to compare this source with other sources, and also to get experimental data which would enable one to explain the mechanism of the passage of atoms of elements into the interelectrode space in this source, a detailed study was made of the spatial distribution of copper during its evaporation as metal in a spark, in a d.c. arc, and in an impulse arc. The photographs obtained of the arc in γ-radiation were photometrically measured in a large number of sections along and across the interelectrode gap; the results of the photometric measurements are represented in the form of isolines which delineate the plasma regions with equal (within the limits of the range chose for the blackening of the photographic plates) densities of the material. The results obtained are reproduced in Fig. 4. As is evident, in contrast to the spark source and the d.c. arc, in the plasma of which

*Similar phenomena have also been observed for sodium salts.

there is observed a sharp heterogeneous distribution of the material passing from the anode, and a scattering of this material toward the side in the spark, such heterogeneity is almost completely absent in the central zone of the interelectrode gap of an impulse arc. The second distinguishing feature of the diagram representing the spatial distribution of elements in the plasma of this source, is the presence in it of a characteristic "protuberance", characterized by enhanced density, and directly related to the material located in the anode crater. It might be thought that in this way there is a periodic "injection" of the molten mass of the test element * into the interelectrode gap of the source. If this assumption were to be confirmed by further and more detailed experimental work, it would clarify a number of the characteristics of the source described, attention to which has been drawn in a previous paper [1], and would open up a way of solving the question of the use of melts in the practice of spectrographic analytical work.

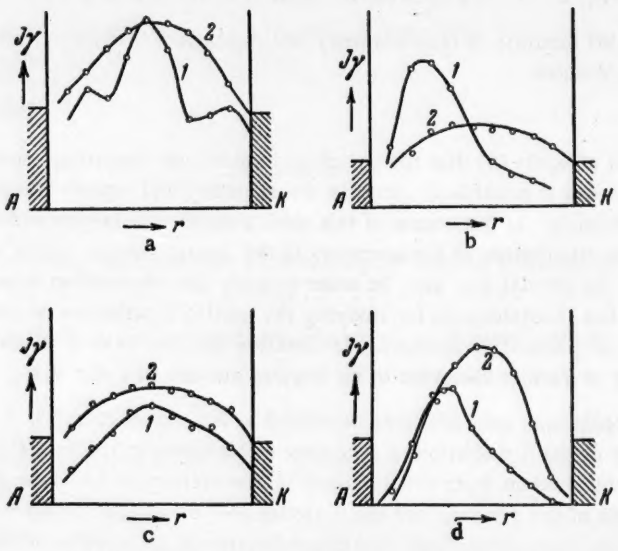

Fig. 1. Distribution of gallium (a), zinc (b), iron (c), and copper (d) in the interelectrode gap of a d.c. arc (1) and impulse arc (2), during evaporation of the elements from their oxides. Labelled atoms Ga^{72}, Fe^{55}, Zn^{65} and Cu^{64}.

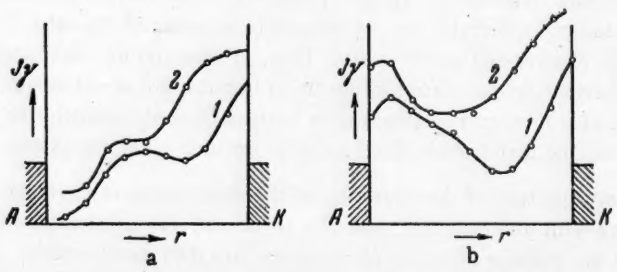

Fig. 2. Distribution of potassium in the interelectrode space of a d.c. arc (1) and an impulse arc (2) during evaporation of the element in the form of K_2CO_3 (a) and K_2SO_4(b). Labelled atom K^{42}

*This mechanism of the passage of elements into the plasma of the source may be occur alongside the usual fractional evaporation.

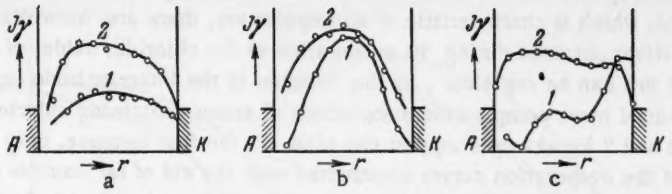

Fig. 3. Distribution of zinc (a), copper (b), and sodium (c) in the interelectrode space of an impulse arc during their evaporation from pure ZnO, CuO, and Na_2CO_3 (1) and from their mixture (2) with graphite and cupric oxide in the proportion 1:1:2.

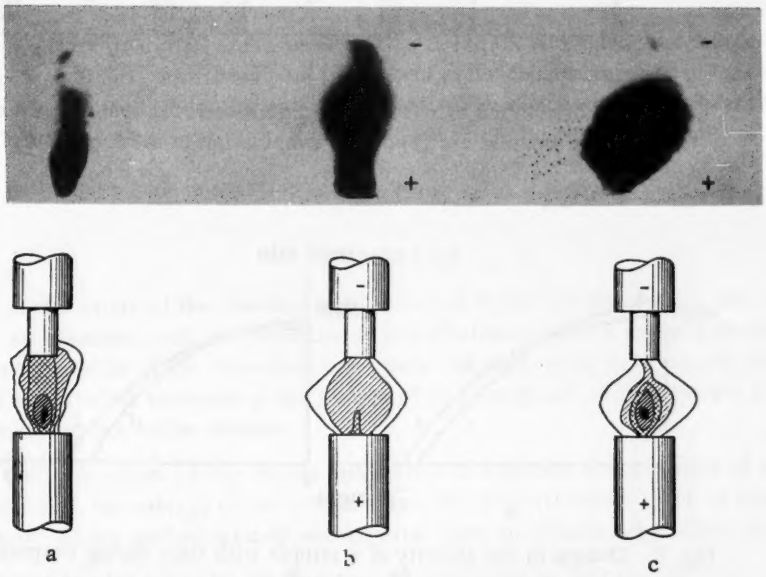

Fig. 4. Photographs of the interelectrode space of a spark (a), an impulse arc (b), and a d.c. arc (c), taken in γ-radiation from Cu^{64}, and the corresponding diagrams representing the distribution of the elements in the plasma of the sources.

The first interesting results which we were able to obtain by using radioactive isotopes for studying the kinetics of the evaporation and distribution of elements in the plasma of various sources, were those obtained on evaporating AgCl. As shown earlier [3], the spatial distribution curves obtained for silver in the interelectrode space of a d.c. arc during the evaporation of this elements as its chloride, oxide, and as the metal itself differ essentially from each other. This testifies to differences in the statein which the test element passes into the arc plasma in the first and in the other two cases, and may be interpreted as indicating that the atoms of silver are not found as simple ions in the plasma.

This question was subjected to additional, and more systematic study, in the work described here. A comparison was made of the curves characterizing the distribution of silver in the interelectrode gap of a d.c. arc and an impulse arc, during the evaporation of this element as the chloride, oxide, and metal (Fig. 5); curves were also obtained for the changes in the activity of the samples with time during evaporation of AgCl with radioactive isotopes of Ag and Cl in both sources (Fig. 6). For comparison, the evaporation curves of Na and S, entering into the composition of sodium sulfate (Fig. 7), were also studied in the same sources by means of radioactive isotopes. The experimental results obtained completely confirm previous observations and show

that, despite the tendency to an increase in the degree of uniformity of the distribution of the elements in the interelectrode space, which is characteristic of an impulse arc, there are, nevertheless, differences in the distribution curves for silver obtained during its evaporation as the chloride, oxide, or metal in this source also. It is very likely that this can be explained , by the presence in the interelectrode space, not of the simplest ions or atoms of silver, but of more complicated associations of atoms containing chlorine atoms. A comparison of the curves in Figs. 6 and 7 for example support this idea. In the first instance, they testify to the almost complete coincidence of the evaporation curves constructed with the aid of radioactive atoms of silver and chlorine, the time of stay of which in the plasma, in this way, proves to be coincident in both sources. In contrast to this, the curves for the change of activity with time for samples containing Na_2SO_4 (Fig. 7), into whose composition radioactive sodium or sulfur enter, differ sharply from each other even on complete dissociation of the salt.

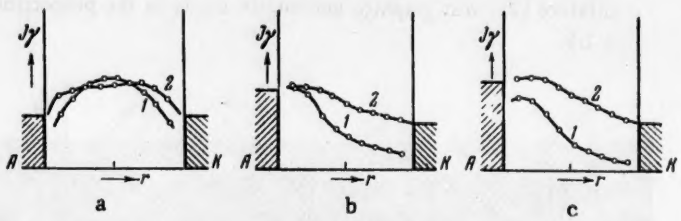

Fig. 5. Distribution of silver in the interelectrode space of a d.c. arc (1) and an impulse arc (2) during evaporation in the form of AgCl(a),

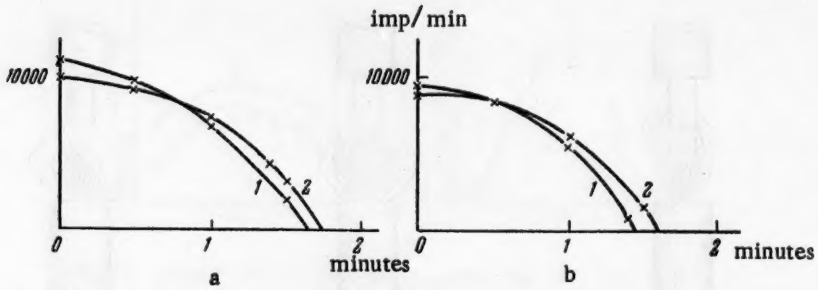

Fig. 6. Change in the activity of a sample with time during evaporation of AgCl with labelled atoms Ag^{110} and Cl^{36} in a d.c. arc (a) and impulse arc (b):
1) Measurements based on Cl; 2) measurements based on Ag.

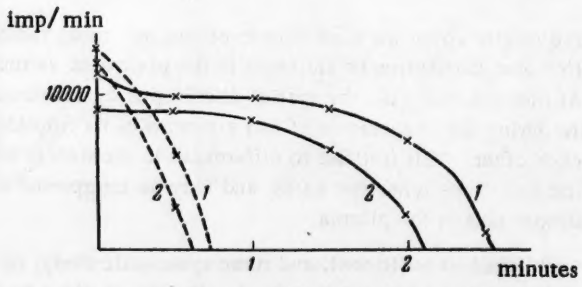

Fig. 7. Change in the activity of a sample with time during evaporation of Na_2SO_4 containing labelled isotopes Na^{24} and S^{35} in a d.c. arc (1) and an impulse arc (2):
Full line for $Na_2{}^{*}SO_4$; dotted line for $Na_2S{}^{*}O_4$

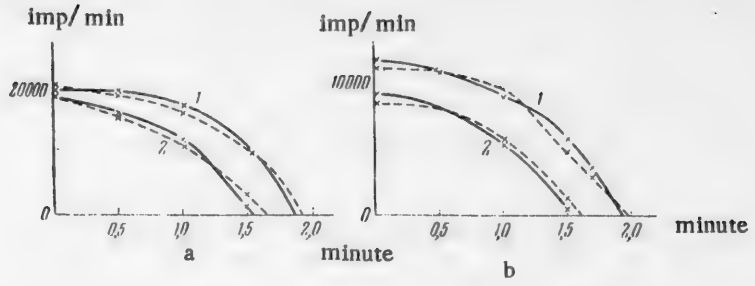

Fig. 8. Change in the activity of a sample with time during the evaporation of NaCl (a) and $CuCl_2$ containing radioactive Na^{24}, Cl^{36}, and Cu^{64} in a d.c. arc (1) and an impulse arc (2): Full line-measurements based on Cl; dotted lines-measurements based on Na and Cu respectively.

As is evident from a consideration of the results shown in Fig. 8, coincidence of the curves for change of activity of the sample with time, constructed with the help of radioactive isotopes of the metal and chlorine, is observed not only for AgCl, but also during the evaporation of the elements entering into the composition of other chlorides. The authors wish to thank N. P. Yakovlev for his help in carrying out the work described here.

SUMMARY

Independently of the nature of the distribution of elements in the plasma of a d.c. arc, in the impulse arc there is observed for all elements, with the exception of the alkaline metals, a uniform distribution with a maximum located in the middle of the interelectrode space. In order to smoothe out the curves for the distribution of atoms of the alkaline elements in the plasma of an impulse arc, it is necessary to dilute samples or salts of these elements with a buffer mixture.

Experimental results obtained for the spatial distribution of elements in the plasma of an impulse arc make it possible to postulate that, the passage of the elements into the interelectrode space of this source is realized by periodic "injections" of the molten mass of test material into the plasma, in addition to the usual fractional evaporation.

A study of the kinetics of evaporation and spatial distribution of elements in the plasma of an impulse arc and of a d.c. arc, taking various compounds of silver, and also the chlorides of silver and copper as test materials, has shown that there is a relationship between the corresponding curves and the type of compound used. This indicates that the atoms of these elements exist in different forms in the source plasma when they are evaporated in the form of different compounds.

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COMPLEXOMETRIC TITRATION WITH METALLO-INDICATORS

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Complexometric titration is widely used in modern analytical chemistry [1]. The properties of the most important complexons and of the complexes which these complexons give with various metal ions have been studied in fair detail [2-4]. The properties of such metallo-indicators as murexide and eriochrome black(chromogen black ET-00) have been studied less fully [5-7], while the study of certain new metallo-indicators has been confined simply to determining their sensitivity to various metal ions [8].

As for the general theory of the analytical application of complexons, the basic precepts advanced by Yatsimirskii [9] have not as yet received any further development, and in this connection therefore, there are so far, no correct ideas regarding the factors which affect the accuracy of certain determinations, and the possibility of successive titration in systems containing different metal ions, or regarding calculations which will ensure a critical choice of new procedures, and a rational self-critical conductance of complexometric determination.

The question of the determination of indicator errors reduces either to an evaluation of the equilibrium concentrations of all colored particles, for equimolar initial concentrations of the ions of the metal and the complexon, or to a calculation of the initial concentration of the complexon which will guarantee a given color intensity. For this purpose it is necessary to use the instability constants of the complexes formed with the metallo-indicator corresponding to a given pH of the system, and also to take into account the possible hydrolysis of all the interacting particles.

Let us take as an example the determination of Ca^{2+} by Schwarzenbach's method [1, p. 55], according to which, at a pH of 12.5 the following concentrations, (c) in moles per liter, hold good: $c_{Ca^{2+}} = 10^{-2}$, $c_{NH_4H_4\pi^-} = c_{NH_4^+} = c_{H_{4\pi}^-} = 3.3 \cdot 10^{-5}$ ($NH_4H_{4\pi}$ -is ammonium purpurate). As a start we shall try to explain what will be the intensity of the color of the system after addition of $c_{Na_2H_2R} = c_{H_2R^{2-}} = 10^{-2}$ (Na_2H_2R is Complexon III). Preliminary calculations * show that at a pH of 12.5, about 39 % of Ca is found in the form of $CaOH^+$ ions, 99.4% of Complexon III in the form of R^{4-} ions, and approximately 97% of murexide in the form of $H_{2\pi}^{3-}$ ions.

The following equilibria occur in solution:

$$Ca^{2+} + H_2O \rightleftarrows CaOH^+ + H^+ \quad pK_1 = 12{,}7 \tag{1}$$

$$CaH_2\pi^- \rightleftarrows Ca^{2+} + H_2\pi^{3-} \quad pK_2 = 5{,}1 \tag{2}$$

$$CaR^{2-} \rightleftarrows Ca^{2+} + R^{4-} \quad pK = 9{,}2 \text{ for } \mu = 0{,}7. \tag{3}$$

*For these calculations the following values were used: pK - 12.7 for hydrolysis of Ca^{2+} ions [10], $pK_3 = 6.16$ and $pK_4 = 10.26$ for the dissociation of ethylenediaminetetracetic acid [11], and $pK_2 = 9.2$ and $pK_3 = 10.9$ for purpuric acid [12].

Let us designate $[H^+] = 10^{-12.5}$ by h, and $c_{H_2\pi^3} = 3.3 \cdot 10^{-5}$ by c_1.

$$c_{Ca^{2+}} = c_{R^{4-}} = 10^{-2} = c,\ [CaOH^+] = x,\ [Ca^{2+}] = y,\ [CaH_2\pi^-] = z,$$
$$[CaR^{2-}] = u,\ [H_2\pi^{3-}] = v,\ [R^{4-}] = t.$$

Using the usual methods for calculating equilibrium [13], we obtain the system of equations

$$hx = K_1 y \quad (4) \qquad c = x + y + z + u \quad (7)$$
$$yv = K_2 z \quad (5) \qquad c = u + t \quad (8)$$
$$yt = Ku \quad (6) \qquad c_1 = z + v \quad (9)$$

which readily reduce to the equation

$$(h + K_1)\, y^3 + [c_1 h + (h + K_1)(K + K_2)]\, y^2 -$$
$$- K\,[h\,(c - c_1) - K_2\,(h + K_1)]\, y - chKK_2 = 0 \quad (10)$$

After substituting the values of known factors and transforming we get the cubic equation

$$y^3 + 2{,}820 \cdot 10^{-5} y^2 - 3{,}851 \cdot 10^{-12} y - 3{,}073 \cdot 10^{-17} = 0,$$

which is readily solved by Horner's method [13]. As a result we find that $y = [Ca^{2+}] = 1.1 \cdot 10^{-6}$, $x = [CaOH^+] = 6.9 \cdot 10^{-7}$, $z = [CaH_2\pi^-] = 4.0 \times 10^{-6}$, $v = [H_2\pi^{3-}] = 2.9 \cdot 10^{-5}$, $u = [CaR^{2-}] = 9.992 \cdot 10^{-3}$ and $t = [R^{4-}] = 5.8 \cdot 10^{-6}$.

The color of the solution is determined by the ratio $v:z = [H_2\pi^{3-}] : [CaH_2\pi^-] = 7.3$. Since the concentration of the blue ions of $H_2\pi^{3-}$ is 7.3 times the concentration of the red ions of $CaH_2\pi^-$, the color of the mixture should be a blue-violet as indicated in Schwarzenbach's procedure.

It must be specially emphasized that $pK_2 = 5.1$ for the instability of $CaH_2\pi^-$, is taken from the special table of Schwarzenbach for a pH of 12.5.

We shall now carry out a similar calculation for the determination of Mg^{2+} ions using eriochrome black-T(NaH_2E) as indicator [1, p. 56]. Transforming the concentrations into moles per liter leads to the values: $c_{Mg^{2+}} = 8 \cdot 10^{-3}$ and $c_{NaH_2E} = 2.5 \cdot 10^{-5}$ (at pH 10). Preliminary calculations lead to the following: at a pH of 10, more than 16% of the Mg is found in the form of $MgOH^+$ ions; 97.3% of the indicator is in the form of NE^{2-} ions, while Complexon III gives 64.5% of HR^{3-} ions and 35.4% of R^{4-} ions. *

On this basis, the initial conditions of the problem, after addition of an equivalent amount of Complexon III, are determined by the following data: pH 10, $c_{Mg^{2+}} = 8 \cdot 10^{-3} = c$, $c_{HE^{2-}} = 2.5 \cdot 10^{-5} = c_1$ and $c_{HR^{3-}} = 8 \cdot 10^{-3} = c$. We get the following equilibria:

$$Mg^{2+} + H_2O \rightleftarrows MgOH^+ + H^+ \quad pK_1 = 10{,}7 \quad (11)$$
$$HE^{2-} \rightleftarrows H^+ + E^{3-} \quad pK_{13} = 11{,}52 \quad (12)$$
$$HR^{3-} \rightleftarrows H^+ + R^{4-} \quad pK_{24} = 10{,}26 \quad (13)$$
$$MgR^{2-} \rightleftarrows Mg^{2+} + R^{4-} \quad pK = 8{,}69 \quad (14)$$

* The following values were used in these calculations: pK = 11.7 for the hydrolysis of Mg^{2+} ions [10, p. 314] and $pK_2 = 6.3$ and $pK_3 = 11.52$ for eriochrome black T [7].

$$MgE^- \rightleftarrows Mg^{2+} + E^{3-} \quad pK_2 = 5 \tag{15}$$

the value of pK_2 is taken from Schwarzenbach's graph at a pH of 10 [5].

The following designations are used $[Mg^{2+}] = x$, $[MgOH^+] = y$, $[HE^{2-}] = z$, $[E^{3-}] = u$, $[HR^{3-}] = v$, $[R^{4-}] = w$, $[MgR^{2-}] = t$, $[MgE^-] = s$; then proceeding according to the general rules [13] we obtain the following system or equations

$$hy = K_1 x \tag{16}$$

$$hu = K_{13} z \tag{17}$$

$$hw = K_{24} v \tag{18}$$

$$xw = Kt \tag{19}$$

$$xu = K_2 s \tag{20}$$

$$c = x + y + t + s \tag{21}$$

$$c = v + w + t \tag{22}$$

$$c_1 = z + u + s, \tag{23}$$

which reduce to the equation

$$hK_{13}As^3 + \{hK_{13}[D - (c_1A - B) - cA] - AE\}s^2 - \\ - \{BE + hK_{13}[c_1(B + D) - c(c_1A - B)]s + cc_1hK_{13}B\} = 0 \tag{24}$$

where

$$A = K_2K_{24}(h + K_{13}) - KK_{13}(h + K_{24}),$$
$$B = c_1KK_{13}(h + K_{24}),$$
$$D = cK_2K_{24}(h + K_{13}),$$
$$E = K_2(h + K_1)(h + K_{13}).$$

After substituting the values of h, c_i, and K_i, and carrying out the usual transformations we get the equation

$$s^3 - 4{,}683 \cdot 10^{-4}s^2 - 1{,}868 \cdot 10^{-13}s + 8{,}441 \cdot 10^{-17} = 0 \tag{25}$$

The first positive root of this equation $s_1 = [MgE^-] = 4.683 \cdot 10^{-4}$ does not satisfy the initial conditions of the problem, since the value of $t = [MgR^{2-}] = 8 \cdot 10^{-3}$ and the sum $s_1 + t \approx 8.5 \cdot 10^{-3}$, calculated by means of it, are greater than $c_{Mg^{2+}} = 8 \cdot 10^{-3}$. An approximate value of the second root $s_2 \sim 4.3 \cdot 10^{-7}$ can be found from the equation $s^2 = 1.868 \cdot 10^{-13}$, while an accurate value can be found by the method of successive approximation. All the equilibrium concentrations are calculated by means of it: $s = [MgE] = 4.245 \cdot 10^{-7}$, $u = [E^{3-}]$

$$u = [E^{3-}] = 7{,}2 \cdot 10^{-7},\ z = [HE^{2-}] = 2{,}4 \cdot 10^{-5},\ x = [Mg^{2+}] = 5{,}9 \cdot 10^{-6},$$
$$y = [MgOH^+] = 1{,}2 \cdot 10^{-6},$$

The color of the equilibrium system is determined by the ratio between the concentrations of the blue HE^{2-} particles, the red MgE^- particles, and the orange E^{3-} ions. In our case

$$\frac{[HE^{2-}]}{[MgE^-] + [E^{3-}]} = \frac{2{,}4 \cdot 10^{-5}}{4{,}2 \cdot 10^{-7} + 7{,}2 \cdot 10^{-7}} = 21,$$

this indicates that the color of the solution after addition of an equivalent amount of Complexon III should be pure blue, as indicated in Schwarzenbach's procedure.

Since, however, a pure blue color should already be obtained at a ratio of $[HE^{2-}]$: $([MgE^{-}] + [E^{3-}]) = 10$, it is obvious that the procedure includes a systematic error. In order to evaluate this error it is necessary to calculate $c_{HR^{3-}}$ so that

$$[HE^{2-}] = 10\ [MgE^{-}] + [E^{3-}]), \tag{26}$$

then the error will be equal to $c_{Mg^{2+}} - c_{HR^{3-}}$. In this case a new unknown appears $c_{HR^{3-}} = \varphi$ and, at the same time, the additional condition (26). Using the same designations as before for the unknown equilibrium concentrations we get a new system of equations which satisfy the equation

$$z = 10\,(u + s), \tag{27}$$

and instead of equation (22) contains the equation

$$\varphi = v + w + t. \tag{28}$$

The new system is solved much more easily than the previous one, and gives the following results: $z = [HE^{2-}] = 2.27 \cdot 10^{-5}$, $u = [E^{3-}] = 6.86 \cdot 10^{-7}$,

$$s = [MgE^{-}] = 1{,}59 \cdot 10^{-6},\ x = [Mg^{2+}] = 2{,}31 \cdot 10^{-5},\ y = [MgOH^{+}] = 4{,}61 \cdot 10^{-6},$$

$$t = [MgR^{2-}] = 7{,}97 \cdot 10^{-3},\ w = [R^{4-}] = 7{,}04 \cdot 10^{-7},$$

$$v = [HR^{3-}] = 1{,}28 \cdot 10^{-6}$$

and, finally

$$c - \varphi = x + y + s - (v + w) = 2{,}7 \cdot 10^{-5}$$

from which the error sought is

$$\Delta = -\ 0.34\%$$

The problem of the successive titration of two metal ions B and M with concentrations $c_B = c_1$ and $c_M = c_2$ is solved by different methods depending on the pH at which the titration is carried out.

Let us assume that at the given pH, hydrolysis of the complexon can be disregarded. Since, (in such cases,) it is necessary to take into account hydrolysis of the metal ions, let us consider the following complex of equilibria

$$BR \rightleftarrows B + R \qquad K_{11} \tag{29}$$

$$B + H_2O \rightleftarrows BOH + H \qquad K_{12} \tag{30}$$

$$MR \rightleftarrows M + R \qquad K_{21} \tag{31}$$

$$M + H_2O \rightleftarrows MOH + H \qquad K_{22} \tag{32}$$

Let us assume that $K_{11} < K_{21}$. In this case it is ion B that will be titrated mainly, while if it is assumed that toward the completion of titration the initial concentration of the reagent $c_R = c_1$, then it can be assumed that $[BR] = (1 - \alpha)c_1$ and $[MR] = \alpha c_1$, where $0 < \alpha < 1$. The following are unkown $[B] = x$, $[BOH] = y$, $[BR] = z$, $[R] = u$, $[M] = v$, $[MOH] = w$, $[MR] = t$ and α. According to general rules we write the system of equations

$$xu = K_{11}z \tag{33}$$

$$hy = K_{12}x \tag{34}$$

$$uv = K_{21}t \tag{35}$$

$$hw = K_{22}v \tag{36}$$

$$z = (1 - \alpha)\,c_1 \tag{37}$$

$$t = \alpha c_1 \tag{38}$$

$$c_1 = x + y + z \tag{39}$$

$$c_2 = v + w + t \tag{40}$$

The solution

$$\alpha = \frac{(-q+1) + \sqrt{(q+1)^2 + 4q(Q-1)}}{2(Q-1)}, \tag{41}$$

where,

$$q = c_2/c_1, \quad Q = K_{21}(h + K_{22})/K_{11}(h + K_{12}), \tag{42}$$

makes it possible to calculate the fraction of complexon α, combined with the second metal ion at the equivalence point. Thus, for the case of the successive titration of Ca^{2+} and Mg^{2+} ions at pH 12.5, $pK_{21} = 8.69$, $pK_{22} = 11.7$, $pK_{11} = 10.59$, and $pK_{12} = 12.7$, and as a result

at q =	10	1	0.1
α =	0.160	0.066	0.054

i.e. even in the system where $c_{Mg^{2+}} = 0.1\ c_{Ca^{2+}}$, the titration error will be greater than 5%.

At low pH values, similar calculations are complicated by the hydrolysis of the complexon, but are simplified somewhat by reduction of the hydrolysis of the metal ions.

Let us assume that in a system where $c_B = c_1$, $c_M = c_2$, $c_R = c_1$, and $K_{11} < K_{21}$, the following equilibria are established at a given pH

$$B + H_2O \rightleftarrows BOH + H \qquad K_{12} \tag{43}$$

$$BR \rightleftarrows B + R \qquad K_{11} \tag{44}$$

$$H_2R \rightleftarrows H + HR \qquad K_1 \tag{45}$$

$$HR \rightleftarrows H + R \qquad K_2 \tag{46}$$

$$MR \rightleftarrows M + R \qquad K_{21} \tag{47}$$

Here the unkowns are [B] = x, [BOH] = y, [BR] = z, [R] = u, [H_2R] = v, [HR] = w, [MR] = t, [M] = s and α, and the following system of equations can be written

$$hy = K_{12}x \tag{48}$$

$$xu = K_{11}z \tag{49}$$

$$hw = K_1v \tag{50}$$

$$hu = K_2w \tag{51}$$

$$su = K_{21}t \tag{52}$$

$$c_1 = x + y + z \tag{53}$$

$$c_2 = t + s \tag{54}$$

$$c_1 = z + u + v + w + t \tag{55}$$

$$t = \alpha[c_1 - (u + v + w)] \tag{56}$$

A solution of this system with respect to α is possible, but it leads to an equation of the third order

$$D[c_1hK_{21}(c_1 + A) + c_2(c_1hK_{21} + AB)]\alpha^3 +$$
$$+ \{hK_{21}(c_1hK_{21} + c_2B)(c_1 + c_2) - D[c_1hK_{21}(c_1 + A) + 2c_2(c_1hK_{21} + AB)]\}\alpha^2 +$$
$$+ c_2B[AD - 2hK_{21}(c_1 + c_2)]\alpha + c_2^2hBK_{21} = 0,$$

where

$$A = K_2(h^2 + K_1h + K_1K_2)/K_1K_2,\ B = K_{11}(h + K_{12}) \quad \text{and} \quad D = hK_{21}$$

For example, in the case of the procedure given by Yu. I. Usatenko and L. I. Mikhailova [14] for the determination of Fe^{3+} by means of Complexon III at a pH of 1-2 in the presence of divalent metal cations, and using a specific indicator for Fe^{+}, $pK_{12} = 2.5$, $pK_{11} = 25.1$, $pK_{21} = 10.59$ (for Ca^{2+}), $pK_1 = 6.16$, $pK_2 = 10.26$, and $h = 10^{-2}$, if it is assumed that the pH is 2. For the case where $c_1 = 10^{-2}$ and $c_2 = 10$, $c_1 = 0.1$,

$$\alpha^3 - 0{,}9997\,\alpha^2 + 4{,}072 \cdot 10^{-14}\,\alpha + 6{,}004 \cdot 10^{-17} = 0; \tag{58}$$

of the two roots of equation (58): $\alpha_1 = 0.9997$ and $\alpha_2 = 7.8 \cdot 10^{-9}$, only the second one is suitable. As a result it follows that

$$z = [FeR^-] \simeq c_1 = 10^{-2}, \quad t = [CaR^{2-}] = 7{,}8 \cdot 10^{-9}, \quad s = [Ca^{2+}] \simeq c_2 = 0{,}1,$$
$$u = [R^{4-}] = 2 \cdot 10^{-20}, \quad w = [HR^{3-}] = 3{,}6 \cdot 10^{-12}, \quad v = [H_2R^{2-}] = 5{,}2 \cdot 10^{-8}.$$

Thus $\beta = t + u + w + v = 5.98 \cdot 10^{-8}$ mole/liter of Complexon III, which leads to an error

$$\Delta = \frac{(5{,}98 \cdot 10^{-8} + 7{,}8 \cdot 10^{-9}) \cdot 10^2}{10^{-2}} = 6{,}8 \cdot 10^{-4} \ \%$$

It is obvious that in other similar cases, the error may be greater.

Since successive titration of metal ions by means of complexons is not always possible, various methods are used for their removal; the method most often used is precipitation, which, in particular, requires calculation excess precipitant which will prevent interaction between the complexon and the precipitated material. Let us assume, for example that before determining Ca^{2+} or Mg^{2+} by means of Complexon III, zinc ions are removed as ZnS, the question is what $[S^{2-}]$ should be, for example at $c_{Na_2H_2R} = 10^{-3}$ and pH 12.5, so that not more than 0.01% of Complexon III will be expended for dissolving the ZnS. It has been shown that at a pH of 12.5, R^{4-} ions predominate, this means [13]

$$ZnS \rightleftarrows Zn^{2+} + S^{2-} \quad 10^{-22,9}$$
$$Zn^{2+} + R^{4-} \rightleftarrows ZnR^{2-} \quad (10^{-16,15})^{-1}$$
$$ZnS + R^{4-} \rightleftarrows S^{2-} + ZnR^{2-} \quad 10^{-6,75}$$

with

$$10^{-3} \quad x$$
$$10^{-3} - 10^{-7} \quad x + 10^{-7} \quad 10^{-7}$$

and, according to the law of mass action $10^{-7}(x + 10^{-7}) = 1.8 \cdot 10^{-7} \cdot 10^{-3}$, from which $x = c_{S^{2-}} = 1.8 \cdot 10^{-3}$, i.e. and S^{2-} excess concentration of $2 \cdot 10^{-3}$ mole/liter should be sufficient for the separation.

It has been suggested [1, p.58] that in a similar way, at pH 10 it should be possible to determine Mg^{2+} ions, after preliminary precipitation of Ca^{2+} as the oxalate. Since calculations show that CaC_2O_4 should dissolve in Complexon III at pH 10, this method gives rise to doubt although Arkhangel'skaya has given a detailed procedure for such a separation [15]. Using Arkhangel'skaya's results it is possible to calculate that, for example, during the simultaneous presence of $2.0 \cdot 10^{-3}$ mole/liter of Ca^{2+} and $1.8 \cdot 10^{-3}$ mole/liter of Mg^{2+}, the system should contain at a pH of 10, $c_{C_2O_4^{2-}} = 5.1 \cdot 10^{-3}$ and $c_{H_2E} = 2.5 \cdot 10^{-5}$. Here again NaH_2E is eriochrome black ET-00 while the $C_2O_4^{2-}$ is hydrolyzed at the most to the extent of 0.02%. In such a system the following equilibria must be taken into account

$$Mg^{2+} + H_2O \rightleftarrows MgOH^+ + H^+ \qquad pK_1 = 10{,}7 \tag{59}$$
$$HE^{2-} \rightleftarrows H^+ + E^{3-} \qquad pK_{13} = 11{,}52 \tag{60}$$
$$HR^{3-} \rightleftarrows H^+ + R^{4-} \qquad pK_{24} = 10{,}26 \tag{61}$$

$$MgR^{2-} \rightleftarrows Mg^{2+} + R^{4-} \qquad pK = 8{,}69 \tag{62}$$

$$MgE^{-} \rightleftarrows Mg^{2+} + E^{3-} \qquad pK_2 = 5 \text{ at pH } 10 \tag{63}$$

$$Mg(C_2O_4)_2^{2-} \rightleftarrows MgC_2O_4 + C_2O_4^{2-} \qquad pK_3 = 0{,}95 \tag{64}$$

$$MgC_2O_4 \rightleftarrows Mg^{2+} + C_2O_4^{2-} \qquad pK_4 = 3{,}43 \tag{65}$$

$$CaC_2O_4 \rightleftarrows Ca^{2+} + C_2O_4^{2-} \qquad pP = 8{,}75 \tag{66}$$

$$CaR^{2-} \rightleftarrows Ca^{2+} + R^{4-} \qquad pK_5 = 10{,}59 \tag{67}$$

$$Ca^{2+} + H_2O \rightleftarrows CaOH^{+} + H^{+} \qquad pK_6 = 12{,}7, \tag{68}$$

since there are indications of the existence of oxalate complexes of magnesium [16].

Using the designations $c_{Mg^{2+}} = 1.8 \cdot 10^{-3} = c$, $c_{C_2O_4^{2-}} = 5.1 \cdot 10^{-3} = c_1$,

$$c_{H_3E^-} = 2{,}5 \cdot 10^{-5} = c_2,\ c_{Ca^{2+}} = 2{,}0 \cdot 10^{-3} = c_3,\ [H^+] = 10^{-10} = h,\ [Mg^{2+}] = x,$$
$$[MgOH^+] = y,\ [HE^{2-}] = z,\ [E^{3-}] = u,\ [HR^{3-}] = v,\ [R^{4-}] = w,$$
$$[MgR^{2-}] = t,\ [MgE^-] = s,$$
$$[Mg(C_2O_4)_2^{2-}] = q,\ [MgC_2O_4] = p,\ [C_2O_4^{2-}] = r,\ [Ca^{2+}] = n,$$
$$[CaR^{2-}] = m,\ [CaOH^+] = l$$

and designating the number of moles of CaC_2O_4 precipitate in 1 liter of solution by Δ, and $c_{HR^{3-}} = \varphi$, at which value the solutions has a pure blue color, we get the following system of equations

$$hy = K_1 x \tag{69}$$

$$hu = K_{13} z \tag{70}$$

$$hw = K_{24} v \tag{71}$$

$$xw = Kt \tag{72}$$

$$xu = K_2 s \tag{73}$$

$$pr = K_3 q \tag{74}$$

$$xr = K_4 p \tag{75}$$

$$nr = P \tag{76}$$

$$nw = K_5 m \tag{77}$$

$$c = x + y + t + s + q + p \tag{78}$$

$$c_2 = z + u + s \tag{79}$$

$$\varphi = v + w + t + m \tag{80}$$

$$z = 10(s + u) \tag{81}$$

$$hl = K_6 n \tag{82}$$

$$c_1 - c_3 = c_4 = 2q + p + r - \tag{83}$$

$$-(n + m + l), \tag{84}$$

here equation (81) is the limiting conditions for a pure blue-colored solution, and equation (83) is obtained by excluding Δ from the material balance equations

$$c_1 = 2q + p + r + \Delta,\ c_3 = n + m + l + \Delta.$$

From equations (81), (79), (70), (73), and (69) we find $z = [HE^{2-}] = 2.3 \times 10^{-5}$, $u = E^{3-}] = 6.9 \cdot 10^{-7}$, $s = [MgE^-] = 1.6 \cdot 10^{-6}$, $x = [Mg^{2+}] = 2.3 \times 10^{-5}$, $y = [MgOH^+] = 4.6 \cdot 10^{-6}$. Equations (74), (75), and (78) lead us to the equations $p = xr/K_4$, $q = xr^2/K_3K_4$ and $t = c_5 - ar(r + K_3)$, where $c_5 = c - (x + y + s) = 1.771 \cdot 10^{-3}$ and $a = x/K_3K_4 = 0.5538$.

From equations (76), (82), (72), and (77) in a similar way we get $n = P/r$, $l = K_6P/hr$, $w = K[c_5 - ar(r + K_3)]/x$ and $m = KP[c_5 - ar(r + K_3)]/K_5rx$. Substitution of all these expressions in equation (83) leads to an equation of the third order with respect to r

$$2hK_5x^2r^3 + hK_3[K_5x(x + K_4) + aKK_4P]r^2 -$$
$$- hK_3K_4(c_4K_5x - aKK_3P)r - K_3K_4P[K_5x(h + K_6) + c_5hK] = 0,$$

which, after substitution of the letter designations by numerical values , and the usual transformations, leads in the given instance to the equation

$$r^3 + 0{,}9623r^2 - 2{,}456\cdot10^{-3}r - 9{,}788\cdot10^{-6} = 0,$$

from which

$$r = [C_2O_4^{2-}] = 4{,}696\cdot10^{-3},\ p = [MgC_2O_4] = 2{,}9\cdot10^{-4},$$

$$q = [Mg(C_2O_4)_2^{2-}] = 1{,}2\cdot10^{-5},$$

$$n = [Ca^{2+}] = 3{,}8\cdot10^{-7},\ l = [CaOH^+] = 3{,}5\cdot10^{-12},\ t = [MgR^{2-}] = 1{,}467\cdot10^{-3},$$

$$w = [R^{4-}] = 1{,}3\cdot10^{-7},\ m = [CaR^{2-}] = 1{,}9\ 10^{-3},\ v = [HR^{3-}] = 2{,}4\cdot10^{-7}$$

and, finally, $\varphi = c + 1.6\cdot10^{-3}$, which amounts to an error of about 88%. It should be emphasized that the magnitude of the error found depends on the accuracy of the constants used for calculation. The errors which arise are connected with the approximately 95% solubility of CaC_2O_4 in Complexon III when working under equilibrium conditions. Presumably, the method could be used after removal of the CaC_2O_4 precipitate or by carrying out the titration in the presence of an organic liquid immiscible with water. The technique recommended by Z. V. Arkhangel'skaya, i.e. titrating to the first blue color is, in general, not suitable for accurate work, while for approximate determinations, the kinetics of the dissolution of CaC_2O_4 in the complexon should be verified by investigation, or a detailed statistical study should be made of the method.

SUMMARY

The application of the theory of ionic exchange for evaluating the accuracy of complexometric titration involving metallo-indicators has been considered, as well as its application to establishing the possibility of carrying out successive titration of two metal ions, and determining one ion after precipitation of the other by a suitable reagent.

Calculations of the color intensity in systems containing equivalent initial concentrations of metal ions and complexons are presented, together with calculations of the initial concentration of the complexon which will guarantee a given color.

A study has been made of the successive titration of two metal ions which react with the same reagent: 1) for a pH at which the hydrolysis of the anion of the complexon can be disregarded, while hydrolysis of both ions is taken into account, and 2) for a pH at which the hydrolysis of the complexon anion and one of the metal ions is taken into account.

General methods are given for calculating the results of complexometric titrations for systems containing masking and precipitating reagents.

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LOW-MELTING EXTRACTING AGENTS IN ANALYTICAL CHEMISTRY

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Extraction of elements in the form of their oxonium salts by means of oxygen-containing solvents is used very often in analytical chemistry practice. Such extraction makes it possible to achieve a fairly complete removal of those elements which are present in the form of hydrophobic anions such as $FeCl_4^-$, $SbCl_6^-$, BiI_4^-, $InBr_4^-$, and others.

For each oxygen-containing solvent, and for each individual element, there exists an optimum acidity ensuring the best extraction when extraction is carried out according to an oxonium mechanism [1]. Thus, gold, in the form of a salt of the bromide anion, is most completely extracted by means of diethyl ether from 0.5-4 N HBr, and indium from 4-6 N HBr, while iron is only extracted to the extent of 70% from 5 N HBr, and is hardly extracted at all from 0.5 N HBr by diethyl ether [2]. In the same way, under various conditions of acidity, elements are also extracted from hydrochloric acid solutions [3]. Iron and gold can be separated by extracting them by means of diethyl ether from 0.5 N HBr, but not from 4-5 N HBr.

Elements which form inorganic complex anions can be extracted at certain acidities not only in the form of oxonium salts, but also in the form of ammonium salts by means of amines.

The optimum acidity for each solvent is determined by the different capacity of the individual oxygen-containing solvents or amines to dissolve in aqueous solutions of acids to form the salts of oxonium or ammine cations. Extraction of elements by means of an oxonium mechanism is usually carried out at fairly high acidities. Ammine cations are very stable, and, accordingly, a weakly acid medium is sufficient for their formation as a rule. It does not follow, however, that all amines can extract salts of inorganic anions from weakly acid media, and that all oxygen-containing solvent require high acidity. Extraction can readily occur at acidities when only part of the solvent is converted into the salt of the oxonium or ammine cation. Since these salts are, usually, readily soluble in water, the acidity which is suitable for extraction is that at which the extracting agent is about 10-20% more soluble in the acid phase than in pure water. It is readily understood that when the acidity is so high that the extracting agent is completely converted into the salt of the corresponding cation and dissolves in the aqueous phase, extraction becomes impossible. Sometimes, however, extraction can still be carried out even under these conditions, when indifferent solvents such as dichloroethane, chloroform and others are added to the extracting solvent. This, for example, is true for the case of the extraction of niobium from concentrated hydrochloric acid media by means of a mixture of methyldioctylamine and xylene [4], and for the separation of niobium and tantalum by extraction with a solution of tribenzylamine and chloroform [5].

By having at one's disposal a selection of various oxygen-containing solvents and amines, it is possible to realize extraction over a wide range of acidities. The latter will be useful for a more successful extraction separation of the elements, since formation of the the requisite complex anions by the various elements, the salts of which are readily extracted, occurs at different acidities. Thus, quadrivalent selenium and tellurium, at low acidities, form hydrophilic anions SeO_3^{2-} and TeO_3^{2-}, while in a medium of concentrated hydrochloric acid tellurium gives a hydrophobic anion $TeCl_6^{2-}$ and the selenium remains in the form of SeO_3^{2-}. This difference has already been used for detecting tellurium in the presence of selenium [6]. Tellurium and selenium, apparently, could be separated by extraction from concentrated hydrochloric acid; during extraction from 6N HCl only 34%

tellurium is extracted and the separation is difficult to carry out [7]. Accordingly, for effective separation of selenium and tellurium it would be useful to have an extracting agent capable of extracting from a medium of concentrated hydrochloric acid, where, for example, diethyl ether is not suitable.

Such considerations could be advanced for a number of other extraction separations. All that has been said emphasizes the desirability of having a choice of extracting agents embracing a wide range of acidities at the disposal of the analyst.

As indicated already [8], for the rapid extraction separation of elements it is very convenient to use solid but low-melting organic materials, or their mixtures with the usual organic solvents, as extracting agents. Such an extraction is carried out in slightly heated solutions when the extracting agent is molten. After extracting and then cooling under the tap, the extracting agent rapidly solidifies into a continuous mass which adheres to the vessel walls, and the aqueous layer can be removed simply by pouring it off. Extraction with low-melting materials does not require the use of a separating funnel.

TABLE 1

Recommended Selection of Low-Melting Mixtures for Extraction of Elements Over a Wide Acidity Range – from pH 3.7 to 18 N ($HCl + H_2SO_4$).
All mixtures contain about 25% paraffin. At 60° they are liquid, at 20° they are semi-solid*

Composition of the mixture	Acidity range for which the mixture is suitable		Efficiency of the mixture, taking extraction of Fe and Cd** as examples	
	Original normality	Equilibrium		
Dimethylaniline + paraffin	1—2	pH 3,7—3,4	20—1,5	Cadmium
α-Naphthylamine	0,3—1	pH 3,6—3,3	70—>70	Cadmium
o-Chloraniline + paraffin	0,1—2	pH 3,7—1,8	2—170	Cadmium
Methyl ethyl ketone + paraffin	0,1—4	0,1—3,3 *N*	6—400	Iron
Cyclohexanone + paraffin	0,1—5	0,1—4 *N*	5—5000—1000	Iron
Diethyl ketone + paraffin	2—9	2—6,4 *N*	10—450 —100	Iron
Methyl butyl ketone + paraffin	4—10	4—7 *N*	15—2000—30	Iron
Methyl isobutyl ketone + paraffin	3—10	3—7,2 *N*	20—2000—200	Iron
Propyl acetate + paraffin	5—8	5—7 *N*	17—75	Iron
Butyl acetate + paraffin	4—9	4—8 *N*	10—75	Iron
Amyl acetate + paraffin	8—11	8—9 *N*	300—500—200	Iron
Ethyl butyrate (the ethyl ester of butyric acid) + paraffin	6—11	6—9 *N*	8—200	Iron
Ethyl isovalerate (the ethyl ester of isovaleric acid) + paraffin	9—20	9—17 *N*	50—500	Iron
Ethyl benzoate + paraffin	10—20	10—18 *N*	>80—1000	Iron

*The volumes of the amines or oxygen-containing solvents taken were equal to the volume of solution being extracted.

**Partition coefficients are given. Where three figures are given the middle one refers to the maximum coefficient observed at an intermediate acidity.

The present article contains a description of a selection of low-melting extracting agents which are suitable for work at varying acidities. The recommended extracting agents were found as a result of a study of the extraction of iron ($FeCl_4^-$) and cadmium (CdI_4^-). Iron and cadmium were chosen because the complex ions indicated are stable over a fairly wide range, so that it was possible to study a wide range of acidities. The good partition coefficients obtained for these elements give a basis for postulating that mixtures are also suitable for the extraction of other elements, as long as the latter are capable of forming readily extractable salts of complex anions in the acidity range studied. Another criterion of the suitability of the mixtures tested for extracting over a given acidity range is the appreciable increase in their solubility – 5-20% – over their solubility in pure water.

Extraction with Mixtures of Oxygen-Containing Solvents and Paraffin

Many liquid esters and ketones which readily extract certain elements, form solid or semisolid mixtures

on addition of a small amount of paraffin (about 25%). These mixtures which readily fuse into a readily mobile liquid on gentle heating, on cooling solidify to a thick mass which adheres to the vessel walls.

The mixtures studied proved to be suitable for the extraction of elements from media with acidities ranging from 0.1-20 N.

During the extraction of iron from 0.1-5 N hydrochloric acid solutions, the chloride ion concentration necessary for the formation of the chloride anion was achieved by addition of a 20% solution of NH_4Cl. The concentration of 20 N in the solution being extracted was established by using a mixture of hydrochloric and sulfuric acids.

Extraction of iron by mixtures of oxygen-containing solvents and paraffin was carried out as follows. To a test tube containing 2 ml of a solution of ferric chloride in hydrochloric acid (or in a mixture of sulfuric and hydrochloric acids) of a definite normality, and containing usually about 5 mg of iron and 400-800 mg of chloride ions, was added 2 ml of the ester or ketone under test, followed by about 0.6 g of paraffin. The latter was melted by heating the test tube in a water bath, and the test tube shaken for 1-2 minutes, the mixture was then cooled under the tap. The aqueous layer was removed from the extract which solidified on the test tube walls, by simply pouring it off; the extract was melted again, and then in order to re-extract the iron, it was shaken with added water. The iron content of aliquots of the aqueous layer and re-extract were determined by means of sulfosalicylic acid, and from the results obtained the partition coefficients calculated. In parallel with this, a sample of the aqueous layer was taken and the equilibrium acidity of the extracting solution determined by titration with 0.1 N potassium hydroxide. As a result of the extraction of some free hydrochloric acid by the solvent, and also as a result of an increase in the volume of the aqueous layer during extraction from fairly concentrated solutions of acids, the equilibrium concentration of the acid was always somewhat lower than the original concentration.

Extraction with Low-Melting Amines or With Mixture of Liquid Amines and Paraffin.

For extracting certain elements from weakly acid, almost neutral solutions, it is possible to use amines; in such cases, the weaker the amine as a base, the more acid the medium it can be used for extracting.

Of the amines tested, the most suitable for extracting elements in weakly acid regions proved to be α-naphthylamine (m.p. 50°) and a mixtures of methylaniline or o-chloraniline with paraffin. The latter, on heating, form homogeneous liquids, while on cooling to room temperature they solidify to give a continuous mass. The extractive capacity of the extracting agents chosen was studied taking as an example the extraction of salts of the iodide anion of cadmium. Extraction was carried out as follows.

Into a test tube with 1 ml of cadmium nitrate solution containing 10 mg of Cd and acidified with hydrochloric acid to the requisite acidity, was added 1 ml of 20% ammonium iodide solution. 2 g of α-naphthylamine or 2 ml of liquid amine followed by 0.6 of paraffin were then added. The test tube was heated on a water bath, shaken for 1-2 minutes, and then cooled. The aqueous layer was poured into another test tube and two aliquots taken from it. The cadmium content of one of the aliquots was determined by colorimetric measurement of the color of the suspension of cadmium sulfide,* while in the other the pH, which differed appreciably from the original pH, was measured.

The results obtained during extraction with mixtures of oxygen-containing solvents or amines with paraffin are given in Table 1.

Recommended Low-Melting Mixtures and Their Characteristics

It is readily seen that the low-melting extracting agents tested make it possible to work over a very wide acidity range, starting at pH 3.7 and ending at 17-18 N, each individual mixture being most suitable for extraction over a particular acidity range (Table 2).

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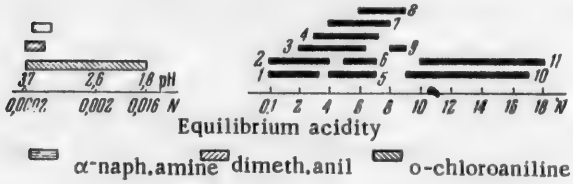
*Since the partition coefficient for CdI_4^{2-} was fairly high in almost all the experiments, and also because of the difficulty of determining cadmium in the organic layer, its content in the latter was not determined, and the partition coefficient was calculated on the basis of the cadmium content of the aqueous layer.

TABLE 2

Acidity Ranges for which Low-Melting Mixtures of Organic Solvent and Paraffin are Suitable



To the left — amines; to the right oxygen-containing solvents

1) Methyl ethyl ketone; 2) Cyclohexanone; 3) Diethyl ketone; 4) Methyl isobutyl ketone; 5) Methyl butyl ketone; 6) Propyl acetate; 7) Butyl acetate; 8) Ethyl butyrate; 9) Isoamyl acetate; 10) Ethyl isovalerate; 11) Ethyl benzoate.

Methods for Preparing the Mixtures

Two methods can be used when using mixtures of organic solvents and paraffin. Three parts of solvent and one part of paraffin can be mixed beforehand on heating, and the solid mixture formed stored in a flask with a ground-glass stopper, a known amount being taken out with a spatula as required. This variant is not very suitable, because on storing for some days there is a tendency to formation of layers. In such an event the mixture should be melted again and cooled prior to use.

In the second variant, the liquid solvent is added directly to the solution to be extracted contained in the vessel to be used for extraction, and a portion of paraffin then added, the amount of the latter being assessed either visually or by approximate weighing. The drawback of this method is that the error involved in only making an approximate estimate of the amount of paraffin added may affect the ease with which the resultant mixture melts, and affect the partition coefficient of the element to be extracted. After some practice, however, a mixture can be prepared fairly rapidly and accurately.

Characteristics of the Mixtures

a) Mixtures of paraffin and amines dimethylaniline or o-chloraniline), and pure α-naphthylamine are suitable for extracting elements from weakly acid media, the equilibrium acidity of which varies within the limits pH 3.7 to pH 1.8. They cannot be used for extracting elements with readily hydrolyzable cations such as: Nb, Ta, Sn, Sb, Fe, and Zr since they are precipitated at low acidities.

α-Naphthylamine and mixtures of o-chloraniline and paraffin are readily oxidized, accordingly iron cannot be extracted by means of them, since under these conditions iron is reduced to the nonextractable divalent state. Because of the ease with which they can be oxidized, the extracting agents described are almost invariably dark in color.

b) Mixtures of paraffin and oxygen-containing solvents. Almost all the recommended mixtures are reasonably stable to oxidizing agents. Mixtures of paraffin and cyclohexanone are exceptional in that they are readily oxidized. Accordingly, such elements as vanadium (V) and chromium (VI) which can only be extracted in higher valence states, are difficult to extract with such a mixture.

Depending on the acidity * of the solution being extracted, the following oxygen-containing solvents, mixed with 25% of paraffin **, are suitable for extraction:

*Equilibrium acidities are quoted.

**In addition to extraction on the basis of an oxonium mechanism, the low-melting mixtures recommended can also be used when extractions of elements based on other mechanisms are carried out.

from 0.1-1 N	Methyl ethyl ketone, cyclohexanone
2N	Methyl ethyl ketone, cyclohexanone, and diethyl ketone
3N	Methyl ethyl ketone, cyclohexanone, diethylketone, methyl isobutyl ketone
4N	Methyl butyl ketone, cyclohexanone, diethyl ketone, methyl isobutyl ketone, butyl butyl acetate
5N	Methyl butyl ketone, propyl acetate, diethyl ketone, methyl isobutyl ketone, butyl acetate
6N	Methyl butyl ketone, propyl acetate, diethyl ketone, methyl isobutyl ketone, ethyl butyrate
7N	Methyl butyl ketone, propyl acetate, methyl isobutyl ketone, butyl acetate, ethyl butyrate
8N	Amyl acetate, butyl acetate, ethyl butyrate
9N	Amyl acetate, ethyl isovalerate, ethyl butyrate
10-17N	Ethyl benzoate, ethyl isovalerate

During the extraction of elements from 0.1-5 N acid solutions, in order to increase the partition coefficients, the ions of the corresponding halide in the form of the ammonium, sodium, or potassium salts should be added to the solution being extracted.

SUMMARY

Solid, low-melting extracting agents facilitate extraction separation of elements, since they permit extraction to be carried out in simple flasks or test tubes, there being no need to resort to the use of separating funnels.

A selection of such low-melting extracting agents is suggested which permits extractions of elements from solutions with acidities ranging from pH 3.7 to 17-18 N. α-Naphthylamine, and a mixture of dimethylaniline or o-chloraniline with paraffin, are suitable for extracting from weakly acid solutions, while starting at 0.1 N acid solutions, a mixture of an oxygen-containing solvent and paraffin is suitable.

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A STUDY OF THE DISSOCIATION OF ARSENAZO (BENZENE-2-ARSONIC ACID - (1-AZO-2)-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULFONIC ACID)

A. E. Klygin and V. K. Pavlova

During the study of the dissociation processes of weak polybasic acids, potentiometric and spectrophotometric methods of investigation are often used; these were the methods that we used in the course of the work described here.

Arsenazo was purified by double recrystallization from an aqueous solution of distilled hydrochloric acid, and dried at room temperature. The percentage purity of the preparation was checked on the basis of its absorption spectra [1].

The stock solution of $4.7 \cdot 10^{-2}$ M arsenazo was prepared by dissolving an exact aliquot of arsenazo. All the measurements of the optical density were carried out on a nonrecording quartz SF-11 spectrophotometer using cells from a photocolorimeter.

Potentiometric titration and measurements of the hydrogen ion concentration were carried out electrometrically on a setup including a PPTV-1 potentiometer, a saturated calomel electrode as the reference electrode and a quinhydrone or glass electrode; in the latter case a LU-2 tube amplifier was used. The accuracy of the measurements was ±0.05 pH units. Experiments were carried out at 20± 0.5°.

All the experimental results were subjected to statistical treatment [2-4] with a confidence level of $\alpha = 0.95$.

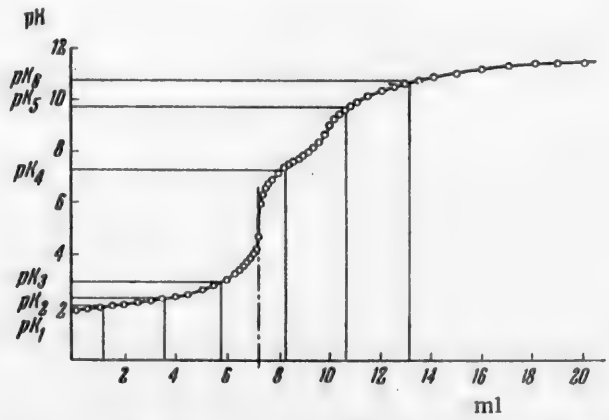

Fig. 1. Potentiometric titration curve of 5 ml of $4.7 \cdot 10^{-2}$M arsenazo solution with $9.79 \cdot 10^{-2}$ M KOH solution.

Potentiometric titration showed that the equivalence point corresponds to the point at which all three hydrogen ions are neutralized. The normality of the stock solution as determined by potentiometric titration was found to be $4.7 \cdot 10^{-2}$ M.

For an approximate evaluation of the pK of the acid, the pH of a solution of acid half neutralized with alkali was used [5].

According to the results of the neutralization curves (Fig. 1), it follows that the order of the first three constants are similar to each other and equal to 10^{-2} - 10^{-3}. The order of the fourth constant differs sharply from the order of the first three constants and from the last two and is given by $K_4 = 10^{-8}$. The values of the last two constants are similar to each other and are of the order of 10^{-11} - 10^{-12}.

The closeness of the values of the first three and the last two dissociation constants of arsenazo did not permit their quantitative determination potentiometrically. Accordingly, further investigations of this reagent were carried out by a spectrophotometric method.

Arsenazo is a weak hexabasic acid. The bright-red color of its aqueous solution changes in relation to the pH, from a raspberry color in alkaline media to a violet in sulfuric and perchloric acid media [6].

Absorption curves for a 2 10^{-5} M solution of arsenazo, taken at various pH's of the solution (Fig. 2), confirmed the effect of the pH of the solution on the positions at which the absorption maxima are located, and on the character of the absorption curve. Spectrophotometric studies of the dissociation processes were carried out on the basis of the results of the curves of "optical density – pH" ("D–pH") at 370, 500, 520, and 570 $m\mu$. This choice of wave lengths made it possible to work at the points of maximum absorption, and in those parts of the spectra which are more sensitive to changes in the concentration of the acid or alkaline forms of the anions of the given dye.

The most noticeable change in the optical density on the five parts of the "D–pH" curves (Figs. 3,4,5) can be explained on the basis of the existence of the following processes:

Section	pH	Reactions	
OR	0— 2	$H_6R \rightleftarrows H_5R^- + H^+$	K_1, ε_1
		$H_5R^- \rightleftarrows H_4R^{2-} + H^+$	K_2, ε_2
AD	2,5— 5,2	$H_4R^{2-} \rightleftarrows H^3R^{3-} + H^+$,	K_3, ε_3
CB	6,5— 9,2	$H_3R^{3-} \rightleftarrows H_2R^{4-} + H^+$,	K_4, ε_4
EF	9,2—11,4	$H_2R^{4-} \rightleftarrows HR^{5-} + H^+$,	K_5, ε_5
NM	11,6—12,5	$HR^{5-} \rightleftarrows R^{6-} + H^+$,	K_6, ε_6

For calculating the molar extinction coefficients (ε) and dissociation constants (K) of the reagent behaving as an indicator, the method suggested by Komar' was used [7].

All calculations were carried out on the basis of measurements of the optical density (D) and the pH of the solutions according to equations (1), (2), (3), and (4), which hold for different experiments at constant wavelength and temperature:

$$K = \frac{(D_l h_l - D_p h_p)(h_l - h_m) - (D_l h_l - D_m h_m)(h_l - h_p)}{(h_l - h_p)(D_l - D_m) - (h_l - h_m)(D_l - D_p)}, \quad (1)$$

$$\varepsilon_n = \frac{(D_l h_l - D_p h_p)(D_l - D_m) - (D_l h_l - D_m h_m)(D_l - D_p)}{Cl\,[(h_l - h_p)(D_l - D_m) - (h_l - h_m)(D_l - D_p)]}, \quad (2)$$

$$\varepsilon_{n+1} = \frac{D_l D_m h_p (h_l - h_m) + D_m D_p h_l (h_m - h_p) - D_l D_p h_m (h_l - h_p}{Cl\,[(h_l - h_m)(D_l h_l - D_p h_p) - (h_l - h_p)(D_l h_l - D_m h_m)]} \quad (3)$$

or

$$\varepsilon_{n+1} = \frac{D_l (K + h_l)}{KCl} - \frac{h_l \varepsilon_n}{K}, \quad (4)$$

where ϵ_n and ϵ_{n+1} are the molar extinction coefficients for ions with charges of n and n + 1; K is the dissociation constant for the reaction $H_{(6-n)} R \rightleftharpoons H_{(6-n-1)} R^{(n+1)} + H^+$; C is the original concentration of arsenazo ($1.4 \cdot 10^{-5}$M); 2 is the cell length (2 cm); $D_{1,\ m,p}$ are the optical densities in experiments 1, m, p; and $h_{1,m,p}$ the hydrogen ion concentrations in experiments 1, m, p. Because there is a slight increase in optical density on sections OR and AD (Figs. 3,4,5), calculations of the values of K_1, K_2, and K_3 did not give positive results for the given series of experiments. Determination of the values of K_4, K_5, and K_6 were carried out on the basis of the results of "D – pH" curves (Table 1) for the parts designated on Figs. 3, 4 and 5 by CB, EF, and NM. Results of these calculations are given in Table 2. The results given in the Table show good agreement between the values given below for K_4, K_5, and K_6 and calculated by various methods for experimental points at different wave lengths, and the values of the molar extinction coefficients ϵ_3, ϵ_4, and ϵ_5 at 500 mμ. This confirms the existence of different forms of the arsenazo anions and the correctness of the method of calculation used.

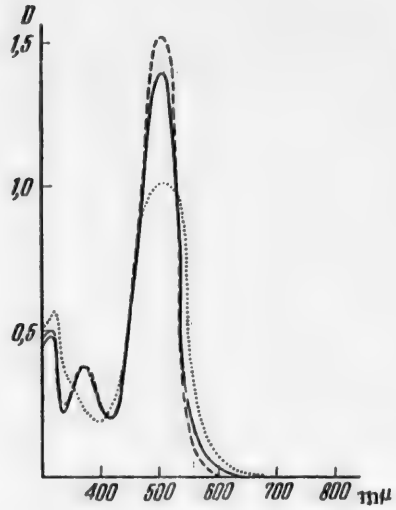

Fig. 2. Absorption curves for $2.4 \cdot 10^{-5}$M arsenazo solution at various pH's
– – – – pH 1.2; ——— pH 6 3 ...10.36.
(cell 3 cm)

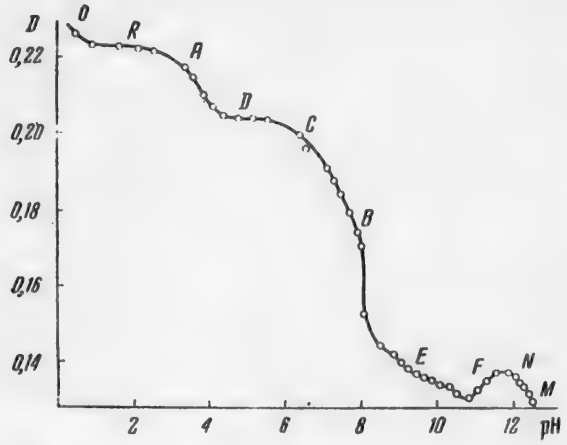

Fig. 3. "D – pH" curve at 370 mμ

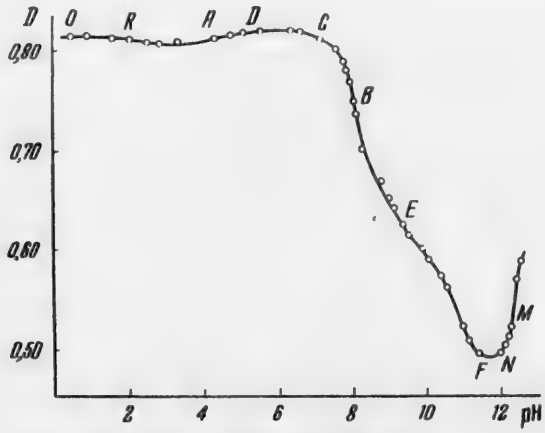

Fig. 4. "D – pH" curve at 500 mμ

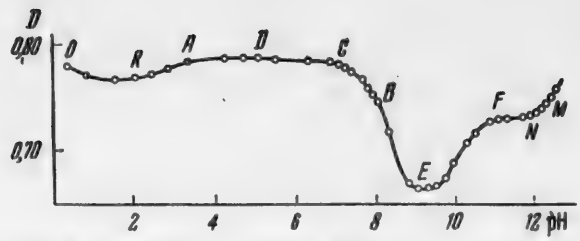

Fig. 5. "D – pH" curve at 520 mμ.

TABLE 1

Results of the "D – pH" Curves at 370, 500, and 520 Taken for Calculation

Nos. / Value	14	15	16	17	18	25	26	27
pH	7,09	7,25	7,45	7,70	7,85	9,50	9,77	10,00
D_{500}	0,814	0,810	0,802	0,790	0,782	0,608	0,600	0,590
D_{520}	0,786	0,783	0,778	0,77	0,765	0,667	0,676	0,688
D_{370}	0,191	0,188	0,184	0,179	0,176	0,137	0,135	0,134

Nos. / Value	28	29	30	33	34	35	36	37
pH	10,35	10,49	10,95	11,90	12,04	12,12	12,22	12,35
D_{500}	0,570	0,559	0,519	0,490	0,498	0,504	0,516	0,566
D_{520}	0,710	0,720	0,730	0,736	0,740	0,741	0,741	0,748
D_{370}	0,133	0,131	0,130	0,137	0,136	0,135	0,134	0,132

TABLE 2

Results of the Calculations of K_4, K_5, and K_6 and of ϵ_4, ϵ_5, and ϵ_6 by Means of Equations (1), (2), (3), and (4)

Calculation for the points	$K_n = \bar{K}_n \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$	$\varepsilon_n = \bar{\varepsilon}_n \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$	$\varepsilon_{n+1} = \bar{\varepsilon}_{n+1} \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$
14, 15, 16, 17, 18 At 370 mμ	$K_4 = (3,3 \pm 0,5) \cdot 10^{-8}$	$\varepsilon_3 = (7,2 \pm 0,07) \cdot 10^3$	$\varepsilon_4 = (5,9 \pm 0,0) \cdot 10^3$
14, 15, 16, 17, 18 At 500 mμ	$K_4 = (1,2 \pm 0,2) \cdot 10^{-8}$	$\varepsilon_3 = (2,9 \pm 0,06) \cdot 10^4$	$\varepsilon_4 = (2,56 \pm 0,07) \cdot 10^4$
14, 15, 16, 17, 18 At 620 mμ	$K_4 = (1,4 \pm 0,2) \cdot 10^{-8}$		
25, 26, 28, 29, 30 At 500 mμ	$K_5 = (2,3 \pm 0,4) \cdot 10^{-11}$	$\varepsilon_4 = (2,2 \pm 0,03) \cdot 10^4$	$\varepsilon_5 = (1,85 \pm 0,02) \cdot 10^4$
25, 26, 27, 28, 29 At 520 mμ	$K_5 = (3,5 \pm 0,4) \cdot 10^{-11}$		
33, 34, 35, 36 At 500 mμ	$K_6 = (3,4 \pm 2,8) \cdot 10^{-13}$	$\varepsilon_5 = (1,6 \pm 0,004) \cdot 10^4$	$\varepsilon_6 = (2,23 \pm 0,03) \cdot 10^4$
33, 34, 36, 37 At 520 mμ	$K_6 = (9,2 \pm 6,5) \cdot 10^{-13}$		

TABLE 3

Results of the "D – pH" Curves at 370 and 570 $m\mu$. Taken for Calculation (The results of these calculations are given in Table 4)

Value / Nos.	1	2	3	4	5	6	7	8	9	10
pH	1,76	2,40	2,63	2,81	3,02	3,27	3,41	4,28	5,50	6,03
D_{370}	1,51	1,48	1,47	1,45	1,43	1,41	1,40	1,34	1,32	1,32
D_{570}	0,406	0,433	0,438	0,443	0,449	0,454	0,460	0,469	0,470	0,481

TABLE 4

Results of Calculations of K_3 and ϵ_2 and ϵ_3 by Means of Equations (1), (2), (3), and (4)

Calculations for the points	$K_3 = K_3 \mp \frac{t_\alpha \cdot \delta}{\sqrt{n}}$	$\epsilon_2 = \bar{\epsilon}_2 \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$	$\epsilon_3 = \bar{\epsilon}_3 \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$
3, 4, 5, 6, 7 At 370 $m\mu$	$(1,9 \pm 0,5) \cdot 10^{-3}$	$(8,24 \pm 0,3) \cdot 10^3$	$(7,3 \pm 0,04) \cdot 10^3$
2, 3, 4, 5, 6 At 570 $m\mu$	$(1,9 \pm 0,8) \cdot 10^{-3}$	$(2,22 \pm 0,02) \cdot 10^3$	$(2,43 \pm 0,03) \cdot 10^3$

TABLE 5

Results of the "D – pH" Curves at 370 Taken for Calculation (Results of the Calculations are given in Table 6)

Values / Nos.	1	2	3	4	5	6	7	8
pH	0,27	0,38	0,51	0,64	0,82	1,05	1,15	1,35
D_{370}	0,392	0,391	0,390	0,389	0,388	0,387	0,386	0,385

A comparison of the "D – pH" curves at wave lengths of 370, 500, and 520 $m\mu$ shows the greatest change in optical density on section AD at 370 and 520 $m\mu$. Determination of the value of K_3 was carried out on the basis of the "D – pH" curves at 370 and 570 $m\mu$ with the highest arsenazo concentration of $9.4 \cdot 10^{-5}$ M. The results are given in Tables 3 and 4.

The values of ϵ_3 at 370 $m\mu$ in Table 4 are in good agreement with the values of ϵ_3 in Table 2; in addition, a comparison of the values of ϵ_2 and ϵ_3 (Table 4) show that the highest value of ϵ_2 is observed at 370 $m\mu$.

Accordingly, determination of the value of the dissociation constants of the first two stages were carried out on the basis of the "D – pH" curves at 370 $m\mu$ for solutions with pH 0.2-1.5 and an arsenazo concentration of $9.4 \cdot 10^{-5}$ M. These results are given in Tables 5 and 6.

As the results in Table 5 show, the values of the optical density hardly change at all over the pH range tested. Nevertheless, by choosing a combination of the points furthest removed from each other, it is possible to get values of the dissociation constant which testify to the existence of two stages of dissociation in this pH range.

TABLE 6

Calculation of K_1 and K_2 and of ϵ_0, ϵ_1, and ϵ_2 by Means of Equations (1), (2), (3), and (4) at 370 mμ

No. of points, i m p	$K_1 \cdot 10^1$ according to (1)	$\varepsilon_0 \cdot 10^{-3}$ according to (2)	$\varepsilon_1 \cdot 10^{-3}$ according to (3)
1,3,5	6,9	8,4	8,3
1,2,4	9,1	8,6	8,4
2,4,5	12,0	8,6	8,4
1,4,5	12,0	8,6	8,0
2,3,5	5,6	8,4	8,2
2,3,4	5,0	8,5	8,0
1,2 5	9,5	8,1	8,1
Mean	$(8,5\pm2,6)\cdot10^{-1}$	$(8,5\pm0,1)\cdot10^3$	$(8,2\pm0,2)\cdot10^3$

No. of points, i m p	$K_2 \cdot 10^2$ according to (1)	$\varepsilon_1 \cdot 10^{-3}$ according to (2)	$\varepsilon_2 \cdot 10^{-3}$ according to (4)
4,5,7	2,7	8,3	
4,6,7	1,0	8,3	
4,5,8	5,7	8,3	8,3
4,7,8	14,8	8,4	8,2
5,6 8	2,5	8,3	8,2
5,7,8	17,2	8,4	8,1
4,6,8	4,7	8,3	8,1
Mean	$(6,9\pm5,9)\cdot10^{-2}$	$(8,3\pm0,08)\cdot10^3$	$(8,2\pm0,09)\cdot10^3$

TABLE 7

Results of Calculating pH and D

Predominant form of the anion	pH value at the change-over point	$D=\varepsilon_n lC$	D, experimental value based on "D–pH" curves
H_5R^-	0,60	$D=0,390$, $l=0,5$ cm 370 mμ, $\varepsilon_1=8,3\cdot10^3$, $C=9,4\cdot10^{-5}$ M	0,390
H_4R^{2-}	1,95	$D=0,385$, $l=0,5$ cm 370 mμ, $\varepsilon_2=8,2\cdot10^3$, $C=9,4\cdot10^{-5}$ M	0,384
H_3R^{3-}	5,20	$D=0,813$, $l=2,0$ cm 500 mμ, $\varepsilon_3=2,9\cdot10^4$, $C=1,4\cdot10^{-5}$ M	0,819
H_2R^{4-}	9,20	$D=0,616$, $l=2,0$ cm 500 mμ, $\varepsilon_4=2,2\cdot10^4$, $C=1,4\cdot10^{-5}$ M	0,624
HR^{5-}	11,40	$D=0,484$, $l=2,0$ cm 500 mμ, $\varepsilon_5=1,73\cdot10^4$, $C=1,4\cdot10^{-5}$ M	0,488

The values of K and ϵ obtained can be used for calculating the values of the optical densities for points corresponding to the regions where any one anion of the dye preferentially exists. In order to calculate the pH at which the given form of the anion exists in maximum concentration, it is necessary to take into account the following processes:

$$H_{(6-n)}R^{n-} \rightleftarrows H_{(6-n-1)}R^{(n+1)-} + H^+,\ K_{n+1}$$

$$H_{(6-n-1)}R^{(n+1)-} \rightleftarrows H_{(6-n-2)}R^{(n+2)-} + H^+,\ K_{n+2}.$$

When the initial concentration of the dye is C (mole/liter), while the equilibrium concentrations are – $[H^+] = h$, $[H_{(6-n)}R^{-n}] = v$, $[H_{(6-n-1)}R^{(n+1)-}] = w$, $[H_{(6-n-2)}R^{(n+2)-}] = z$, then

$$K_{(n+1)}v = wh \tag{5}$$

$$K_{(n+2)}w = zh \tag{6}$$

$$C = v + w + z \tag{7}$$

Differentiating equations (5), (6), and (7) with respect to h and equating w' to 0, we get the system of equations:

$$K_{(n+1)}v' = w \tag{8}$$

$$z'h + z = 0 \tag{9}$$

$$v' + z' = 0 \tag{10}$$

By substituting the values of v', z', and z found from (8), (9), and (6) in (10) we find that

$$h = \sqrt{K_{(n+1)}K_{(n+2)}}. \tag{11}$$

Results of the calculations of pH and D given in Table 7 show good agreement between the values of optical density obtained experimentally and by calculation.

SUMMARY

The six stages of arsenazo dissociation have been studied, and the values of the dissociation constants and molar extinction coefficients determined (at 370, 500, 520, and 570 m μ).

It has been shown that it is more expedient to use a spectrophotometric method of study for determining the successive dissociation constants of weak organic acids when these constants lie close to each other, provided the corresponding forms of the anion have different molar extinction coefficients.

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A SPECTROPHOTOMETRIC STUDY OF THE COLORED COMPLEXES OF QUADRIVALENT TIN WITH CERTAIN REAGENTS CONTAINING OH GROUPS

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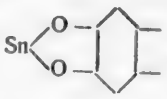
Color reactions and methods for the photometric determination of quadrivalent tin are usually based on the formation of compounds with colored reagents. The light absorption of such compounds is determined by the addendum and not by the central ion of the complex. Colored compounds of tin with alizarin [1], quinalizarin [2], hematoxylin [3], morine [4], quercetin [5], stilbazo [6], hematein [7], and anthrapurpurin and flavopurpurin [8] have been described. All these reagents contain at least two hydroxyl groups in the ortho position.

Nevertheless, as yet, no general criteria for choosing the best of a number of color reagents have been worked out; neither has a comparative study been made of the reagents for tin. We have tried to fill this gap on the basis of a spectrophotometric study of the reactions.

The most important characteristics of a colored complex are its stability and optical properties. Most of the reagents listed above give complexes of reasonable stability with tin. In all cases a chelate bond, develops most often of the type  with a five- membered ring. Accordingly, the complexes of tin with various reagents do not differ very strongly with respect to stability. On the other hand, the effect of complex formation on the conjugation bond of the dye depends essentially on the structure of the latter. The optical effect observed on substituting hydrogen atoms by tin is very strongly developed for various agents.

A comparative study of a series of reagents for tin shows that the optical characteristics are the most important criteria for choosing a reagent of a given type. The sensitivity of a reaction can usually be expressed by the molar light-absorption coefficient (E) of the complex. In addition, the sensitivity and accuracy of a determination depend on the difference between the absorption spectra of the molecular form of the reagent HR and its complex with tin SnR. Finally, the color of all the reagents listed increases (even in the absence of tin) on increasing the pH to a certain limit; accordingly, of great importance is the interval between the pH at which the complex is formed and the pH at which the ionic form (salt) of the dye R^- is formed, the latter being usually intensely colored.

Colored Compounds of Tin with Hydroxyanthraquinones.

The reagents tested were alizarin, quinizarin (1-4-dihydroxyanthraquinone), and quinalizarin (1, 2, 5, 8-tetrahydroxyanthraquinone). Under normal conditions, alizarin forms a very weakly colored compound with quadrivalent tin; its formation is only observable when excess alizarin is extracted with nonaqueous solvents, for example ether.

The compound of tin with quinizarin has an orange color and is sparingly soluble in water, but it can be kept in the form of a colloidal suspension by means of gelatin. The compound is stable at a pH of 4-5. The

difference between the optical densities of a solution of the complex and of free quinizarin is insignificant and does not amount to more than 10%. Accordingly, quinizarin cannot be used as a reagent for the photometric determination of tin.

The complex compound of tin with quinalizarin has been described before [9]. For a light-filter with $\lambda_{Eff.}$ = 496 mμ, the value of the molar coefficient of light absorption of the molecular form of quinalizarin $E_{HR} = 5 \cdot 10^3$, and of the complex $E_{SnR} = 2 \cdot 10^4$. The great drawback of quinalizarin as a reagent is its extremely low solubility in aqueous solutions. On addition of acetone or alcohol, the solubility of quinalizarin and of its complex with tin increases, on the other hand the difference between the absorption spectra of the reagent and of the complex decreases. Finally, another drawback of quinalizarin is the superposition of its indicator properties: the SnR complex is formed only on increasing the pH to 5-6, while at pH 6 formation of the R^- form of quinalizarin starts.

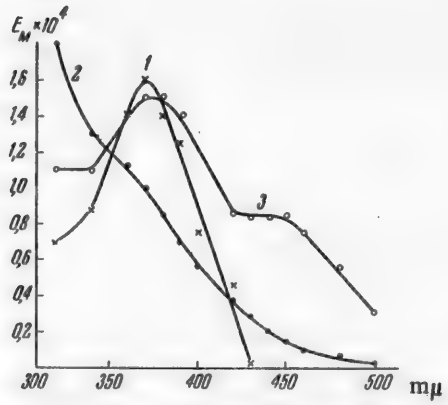


Fig. 1. Absorption spectra of various forms of quercetin:
1) Molecular form (HR); 2) ionic form (R^-); 3) the complex of quercetin with tin (SnR).

The Compound of Quadrivalent Tin with Quercetin

Photometric determination of tin by means of quercetin, according to Liska [5], can be carried out in a solution which is 0.2 N with respect to HCl. The light absorption of solutions of the complex compound formed between tin and quercetin conforms to the Lambert-Beer law. At high tin concentrations it is necessary to construct a calibration curve. According to the same source there is formed a compound with a ratio of tin to quercetin of 3:2.

We used quercetin obtained from onion peel *. Quercetin is sparingly soluble in water but readily soluble in alcohol. The compound of quadrivalent tin with quercetin is also sparingly soluble in water but is considerably more soluble in alcohol. Accordingly, the reaction between Sn^{IV} and quercetin was studied in 50% alcoholic solutions. In acid media at a pH of 1-8, quercetin solutions are colored pale-yellow. At pH ≥ 10 the solubility of quercetin increases and the solutions acquire a bright-yellow color. When such solutions are stood in air the quercetin breaks down and the color of the solutions gradually becomes pale. Formation of a complex of tin with quercetin at concentrations of the components of about $5 \cdot 10^{-5}$M is already observable at a pH of 2 and lower. Nevertheless, on increasing the pH of the solution, the optical density increases several times and attains a constant value at pH 3. Only at pH > 10 does the complex break down appreciably.

Visually, the R^- form of quercetin is similar in color to the SnR form, although the first is considerably weaker in color. This corresponds to the usual relationship. This analogy between the colors of the MeR- and R- forms serves as a physical basis for the theory of "intramolecular dissociation" and for a number of hypotheses regarding the choice of the optimum pH in similar reactions. Nevertheless, a full study reveals a number of characteristics.

In Fig. 1. are shown the absorption of the HR-, SnR-, and R- - forms of quercetin; the curves were obtained by means of a SF-4 spectrophotometer. In the visible part of the spectrum (λ 420 mμ) the absorption curves of the R- and SnR- forms are similar. Nevertheless, the complete absorption spectrum of the R- form (Curve 2) clearly differs from the spectrum of the SnR- form (Curve 3), and is more like the spectrum of the HR-form (Curve 1).

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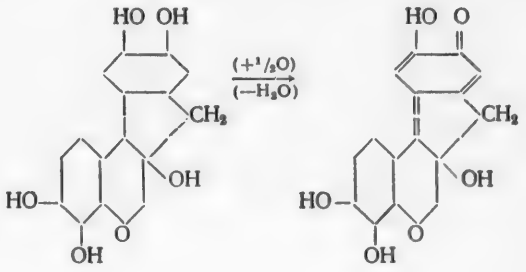
*50 g of onion peel was treated with 100 ml of alcohol and boiled for 2 hours under reflux. The alcoholic solution was poured into 2 liters of water when the quercetin separated out as an orange precipitate. The precipitate was filtered off, dissolved in alcohol and reprecipitated with water. The precipitated quercetin was treated with dilute sulfuric acid on gentle warming. During this state the quercetin separated out as a lemon-yellow precipitate. The precipitate was dried in air. The yield was about 0.3 g of quercetin. This amount of quercetin is sufficient for carrying out about 200 determinations of tin. The commercial preparation of quercetin at our disposal did not give the reaction described with tin.

The results given in Fig. 1 show that for the photometric determination of tin only the visible part of the spectrum can be used. At wave lengths longer than 420 $m\mu$ the molecular HR-form of quercetin absorbs light very weakly, while the complex SnR has a wide absorption band. In the range 420-450 $m\mu$ the molar absorption coefficient of the complex $E'_{SnR} = 8400$, which characterizes the high sensitivity of the reaction.

A Study of the Reaction of Quadrivalent Tin with Hematoxylin

According to Tartakovskii's results [3] the compound of quadrivalent tin with hematoxylin is stable in acid media. This permits the determination of tin in the presence of aluminum and iron, the lakes of which are unstable in acid media. When solutions of hematoxylin are allowed to stand in air, oxidation of the hematoxylin with formation of hematein occurs [10, 11].



This process speeds up appreciably in ammoniacal media [10]. In studying complex formation between hematoxylin and quadrivalent tin, it is of primary importance to establish which of the two forms — hematoxylin or hematein — reacts with tin. Experiments were therefore carried ou both with freshly prepared 10^{-3} M aqueous solutions of hematoxylin, and aqueous solutions which had been allowed to stand for about one month.

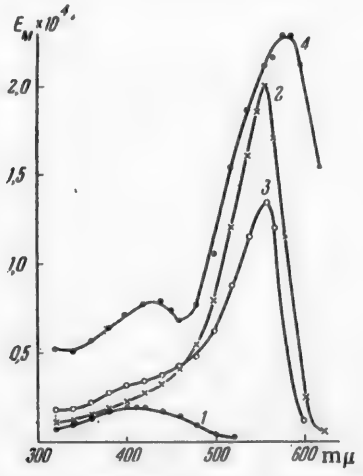


Fig. 2. Absorption spectra of the different forms of hematoxylin: 1) Molecular form (HR); 2) ionic form of hematein; 4) complex with tin (SnR).

Some spectrophotometric characteristics are given in Fig. 2. From this it is evident that in the course of one month, the 10^{-3} M solution of hematoxylin is almost completely oxidized into hematein. The hematoxylin solution as well as the solution of hematein were added to appropriate buffer solutions; in order to study the properties of the complex, the appropriate solutions were mixed so that the total tin concentration was $2.5 \cdot 10^{-5}$, and that of the reagent $5 \cdot 10^{-5}$. 1 ml of a 0.5% freshly prepared solution of gelatin (was added as a stabilizer) per 10 ml of the total volume of solution.

The effect of the pH on the optical density of the solutions is manifested as follows. Free hematoxylin and hematein absorb light weakly at pH < 8. At pH about 8 the color of the solutions increases sharply; at the same time the irreversible oxidation of the reagent is accelerated. Formation of a complex with tin starts in acid media, under these conditions, however, the optical density of the solutions is strongly dependent on the acidity. Formation of a colored complex almost ceases at pH ≥ 2. On increasing the pH further the optical density does not change appreciably. Only at a pH of 9 is there observed a breakdown of the complex with the same effect as that described above for the free reagent. The optimum pH values for photometric determinations are pH 2-6 (see Fig. 6 also).

Some of the spectrophotometric characteristics are shown in Fig. 2. Hematoxylin at a pH of 3 (Curve 1) weakly absorbs light in the short-wave part of the spectrum. The absorption spectra of the ionic forms (R^-) of

hematoxylin (Curve 2), and of hematein (Curve 3), measured at a pH of 8, are similar to the absorption spectrum of the complex SnR with hematein, this corresponds with the relationship normally observed. The SnR complex has one weaker band at 420 mμ; the absorption here is stronger than for the HR- and R- forms of the reagents. For photometric determination it is best to use the optical density at 590 mμ, where the HR-form of the reagent hardly absorbs light at all, while the complex SnR is characterized by a very strong absorption band. At pH < 6, the ionic form of the reagent is hardly formed at all, and, accordingly, the indicator properties of the reagent have no effect.

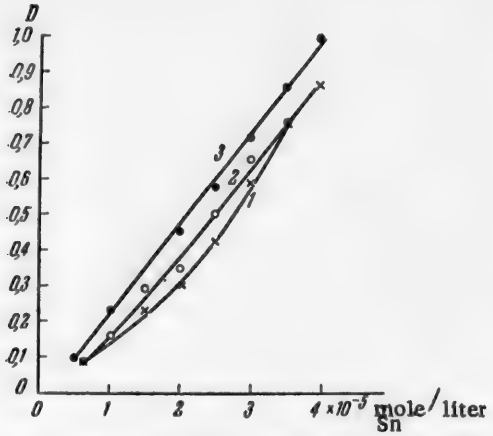


Fig. 3. Relation between the light absorption of solutions of the complex compound of tin with hematoxylin, and tin concentration:
1) with a freshly prepared solution of hematoxylin; 2) with a solution of hematoxylin allowed to stand for 6 days; 3) with a solution which has stood for 2 weeks.

Time during which the solution is allowed to stand does not have a marked qualitative effect on the determination; nevertheless, this time must be taken into account when calibration curves are constructed. In Fig. 3, are shown curves used for the photometric determination of tin by means of a hematoxylin solution, the latter having been allowed to stand for various times before use. When the reagent is allowed to stand beforehand, the sensitivity of the reaction increases somewhat. Solutions of the reagent which have been allowed to stand for two weeks (or more) prior to use were found to conform more closely to Beer's law.

An important advantage of hematoxylin as a reagent for quadrivalent tin, is the fact that neither antimony, or iron form colored complexes with hematoxylin at a pH of 2-3. This fact considerably simplifies the determination of tin.

A Study of the Reaction of Quadrivalent Tin with Stilbazo

According to the results of Kuznetsov et al [6], stilbazo in a weakly acid medium reacts with quadrivalent tin to form a compound with an orange-red color.

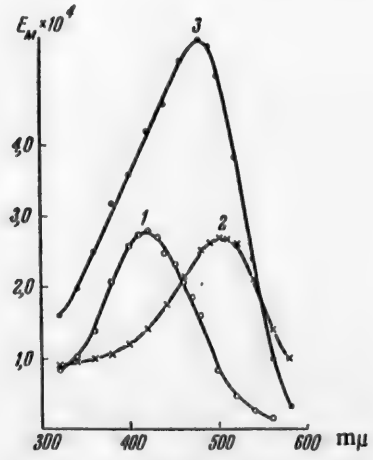


Fig. 4. Absorption spectra of the various forms of stilbazo:
1) The molecular form of stilbazo (HR); 2) the ionic form (R-); 3) the complex with quadrivalent tin (SnR).

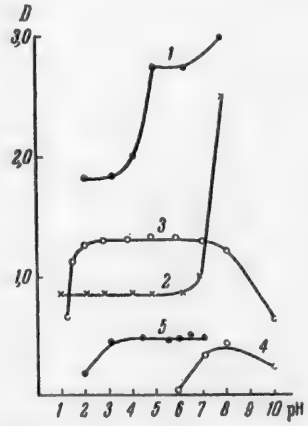


Fig. 5. Effect of pH on complex formation in the system Sn(IV)—organic reagent.
1) The relation between the optical density of solutions of complex of tin and stilbazo, and the pH; 2) solution of stilbazo; 3) solution of the complex of tin with hematoxylin; 4) solution of hematoxylin; 5) solution of the complex of tin with quercetin.

The stock solutions we used were a 10^{-3} M solution of $SnCl_4$ in 1 M hydrochloric acid, and a 10^{-3} M aqueous solution of stilbazo obtained from IREA. *

In Fig. 4 are given the absorption spectra of the HR-, R-, and SnR-forms of stilbazo. Using the isomolar series method, it was established that the composition of the compound formed between quadrivalent tin and stilbazo corresponds to a ratio of the components tin: stilbazo = 1:2. The maximum on the curves is clearly defined, this indicates that the complex is stable.

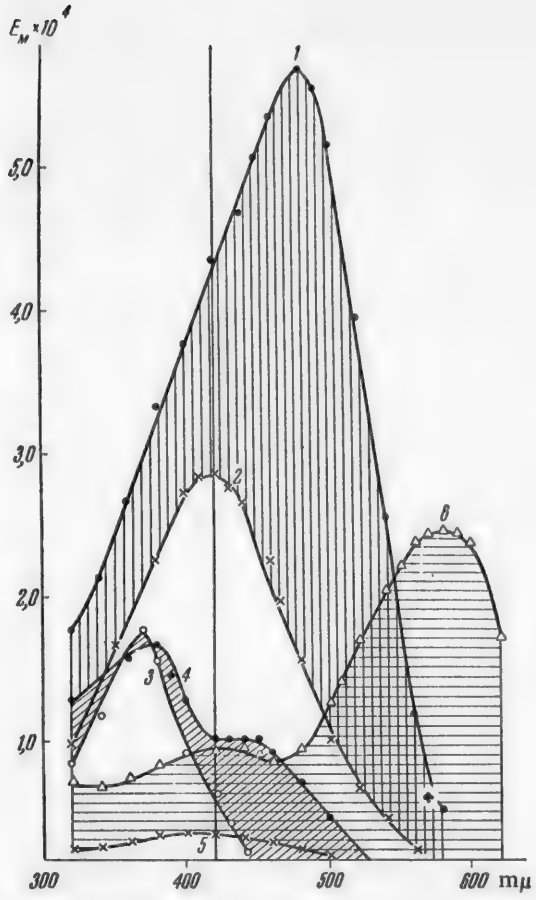


Fig. 6. Absorption spectra of the complex compounds of tin with various OH-containing reagents:
1) The complex of tin with stilbazo; 2) stilbazo; 3) quercetin; 4) complex of tin with quercetin; 5) hematoxylin; 6) the complex of tin with hematoxylin.

Results for the effect of the pH on the light absorption of solutions of the complex compound of tin with stilbazo, and of free stilbazo are given in Fig. 5, for $\lambda_{Eff.}$ = 496 mμ. Formation of a complex compound of tin with stilbazo reaches a maximum at pH 5-7. Stilbazo reagent at a pH of about 6 changes into an ionic R- form which is red in color.

It is clear from Fig. 6 that the indicator properties of stilbazo are a serious hindrance to the use of this reagent in photometry. Qualitative detection of tin is possible within the limits pH 2-6, particularly at a pH of about 6. Nevertheless, in contrast to quercetin and hematoxylin, here small pH variations always show an appreciable effect on the optical density of the solutions. In addition, the intrinsic color of the reagent is signficant, since even even at the optimum pH of about 6, the optical density of a solution of the complex is only twice the optical density of the free reagent (at $\lambda_{Eff.}$ = 440-460 mμ).

Comparison of the Reagents

Of the reagents considered above the most sensitive are quercetin, hematoxylin (oxidized form) and stilbazo. In order to compare these reagents we compared the absorption spectra of the HR- and SnR forms, as shown in Fig. 6. All results are given in E units so that it is possible to compare the reagents independently of the concentration conditions.

The most characteristic criterion is the integral difference between the light absorption of the colored complex SnR and free dye HR; this difference corresponds to the area bounded by the absorption spectrum curves of HR and SnR. In Fig. 6 these characteristic areas are shaded with vertical lines for stilbazo, by horizontal lines for hematoxylin, and by slanting lines for quercetin. By using millimeter tracing paper or by weighing out the pieces of paper cut out in accordance with the areas in Fig. 5., it is possible to compare the absolute and relative differences of the light absorption of the HR- and SnR- forms of the various reagents. The common vertical line separates the visible part of the spectrum. The results given in Fig. 6 show that of the reagents considered, stilbazo is the most sensitive for the qualitative detection of tin.

*The reagent issued by "Soyuzreaktivsbyt" contains an impurity which completely distorts the reaction with quadrivalent tin,. The reaction for tin can only be carried out after purification of the reagent [12].

During the detection of tin by means of this reagent it is essential (and posible) not to use excess stilbazo,otherwise its own light absorption may complicate observations, and any conclusions which may be drawn. During the photometric determination of tin it is essential to use excess reagent, accordingly its own light absorption will become a serious hindrance. It is also important to point out that in the case of stilbazo, the color of the reagent itself is superimposed on the color of the complex in all parts of the spectrum.

Hematoxylin is a somewhat less sensitive reagent. The integral difference in the light absorptions of the HR- and SnR-forms of the reagent is approximately half that for stilbazo. Nevertheless, from the point of view of quantitative photometric determination, hematoxylin has important advantages, since the light absortion of the reagent itself, is insignificant in comparison with the light absorption of the complex. In the region $\lambda >$ $> m\mu$, the free reagent hardly absorbs light at all.

Quercetin is even less sensitive, never theless, for the photometric determination of tin it has the same advantages as hematoxylin. It is essential to point out that quercetin is readily prepared in any laboratory.

It was pointed out above that the indicator properties of a reagent are of particular significance when making a choice of reagent, particularly when there is the possibility of the superposition of the color of the R-form on the color of the complex SnR. In Fig. 5 is shown the relationship between the optical densities of the free reagents, and also of their complex with tin, and the pH of the solution. It is evident from Fig. 5. that the relationship under discussion is most favorable for quercetin, since the free reagent, in the chosen part of the spectrum, in general, does not absorb light. The color of the complex is stable at a pH of 3-6. Thus,random changes in pH of the test solutions have the least effect when quercetin is used.

The color of the complex compound of tin and hematoxylin also changes little at pH 2-6, while superposition of the color of excess reagent can only occur at pH > 6.

Reagent	λ_{max}	E_k (complex)	E_r (reagent)	$E_k - E_r$	$E_k : E_r$	pH range
Quercetin	450	$0.84 \cdot 10^4$	Does not absorb	$0.84 \cdot 10^4$	∞	3-6
Hematoxylin	580	$2.28 \cdot 10^4$	" " "	$2.28 \cdot 10^4$	∞	3-6
Stilbazo	500	$5.00 \cdot 10^4$	$8.7 \cdot 10^3$	$4.13 \cdot 10^4$	5.6	5-6

Conditions for the Photometric Determination of Tin

On the basis of the results obtained, it is possible to give the optimum conditions for the photometric determination of tin by means of the reagents tested.

Determination of tin by means of quercetin should be carried out a a pH of 3-5 in 50% alcoholic solution. Measurements of the light absorption of the tin-quercetin complex can be carried out in a FM-1 photometer using light-filter 7 ($\lambda_{Eff.}$ 465 $m\mu$). 1-15 γ of tin in 15 ml of solution can be determined. The disadvantage of quercetin, like most other reagents for the photometric determination of tin, is the fact that it forms colored compounds with a number of elements, including antimony and iron. These two elements are the ones which accompany tin most often. A study of the effect of various complexing agents as masking agents, such as tartrates, oxalates, fluorides, and Complexon III did not yield the desired results. All these materials form colorless complex compounds with tin, thereby weakening the color of the solutions of the complex of tin with quercetin. For antimony contents equivalent to those of tin, determination of tin by means of quercetin is possible, since antimony under these conditions does not give an appreciable color with quercetin. The effect of iron during the photometric determination of tin with quercetin can be elmiminated by reduing iron to the divalent state by means of thiourea.

Photometric determination of tin with hematoxylin should be carried out at pH 3-5. 5-10 γ of tin in 15 ml of solution can be determined. The concentration of the hematoxylin solution used should be 0.06%. 0.5 ml of this solution is taken for one determination. Light absorption is measured on a FM-1 photometer fitted with a No. 4 light-filter ($\lambda_{Eff.}$ = 574 $m\mu$).

Tin is determined photometrically with stilbazo at a pH of 5. The pH of both the standard and test solutions

must be strictly controlled. The concentration of the stilbazo reagent used is 0.05%. 0.5 ml of reagent solution is taken for one determination. 3-10 γ of tin can be determined in 15 ml of solution. Interference from iron can be suppressed by addition of a saturated solution of thiourea to the solution. Light absorption is measured on a FM-1 photometer using a No. 6 light-filter ($\lambda_{Eff.} = 496\ m\mu$).

SUMMARY

A comparative spectrophotometric study has been made of some hydroxyanthraquinones, quercetin, hematoxylin, and stilbazo as possible reagents for quadrivalent tin. The criteria used for making a choice of a suitable reagent was the integral difference between the light absorption of the colored complex SnR and the free dye HR, and also the difference in the pH range between complete formation of the colored complex and the transition of the dye into the ionic form R^-.

It has been shown that stilbazo is the most sensitive reagent for the qualitative detection of tin. Quercetin and hematoxylin are the most suitable reagents for the photometric determination of tin. Comparative data on the sensitivity of these reagents is given, together with the optimum pH conditions for carrying out the reactions for quadrivalent tin.

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HIGH-VOLTAGE ELECTRODIALYSIS

COMMUNICATION 2. THE REMOVAL OF IMPURITIES FROM METASTANNIC ACID*

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It was shown in a previous article [1] that during the electrodialysis of silicic acid, Fe, Cu, Pb, and Cd present as impurities to the extent of 10^{-2} - 10^{-3}% in the original material can be removed quantitatively down to the limits of the sensitivity of the spectrographic method (about 10^{-4}%). This result was in agreement with results published previously by V. L. Kargin and M. A. Matveeva [2].

It was of interest to examine the possibility of carrying out quantitative separation of metals present as impurities in metastannic acid, gels of which exhibit high absorption properties and trap most cations during precipitation. We carried out tests on the electrodialysis of metastannic acid containing the impurities indicated above to the extent of 10^{-1}%. In addition we carried out tests on the separation of unweighable amounts (traces) of active lead ThB and also of active antimony Sb^{125} in order to assess the possibility of removing impurities under these conditions.

TABLE 1

Spectrographic Analysis of Metastannic Acid Precipitates after Dialysis

Initial content of Fe, Cu, Pb, and Cd (before dialysis) $1 \cdot 10^{-1}$ %

Metal	Method of Preparation	
	First method	Second method
Fe	$1 \cdot 10^{-1}$	$2 \cdot 10^{-2}$
Cu	$0.74 \cdot 10^{-1}$	$8 \cdot 10^{-2}$
Pb	$1 \cdot 10^{-1}$	$8 \cdot 10^{-2}$
Cd	$1 \cdot 10^{-1}$	$5 \cdot 10^{-2}$

*Treatment of metallic tin with concentrated HNO_3.

**Precipitation of Sn^{IV} hydroxide with ammonia.

When dealing with weighable amounts of impurities, preparation of the samples of metastannic acid was carried out as follows.

First Method

An aliquot of metallic tin (usually 1 g) was dissolved in a few ml of concentrated HNO_3 containing 1 mg each of the impurities indicated (in terms of the metal) in the form of their nitrates.

Second Method

An aliquot of metallic tin (1 g) was dissolved in concentrated HCl, and the divalent tin oxidized by means of iodine solution; to the solution thus obtained, 1 mg each of the impurities indicated above were added (in the form of nitrates), and the hydroxides precipitated by means of concentrated ammonia. In both cases the suspension of metastannic acid formed was freed from excess electrolytes by means of centrifuging or filtration on a glass filter under suction, and consequent washing of the precipitate with hot water.

When the first method was used more dense precipitates were obtained, while when the second method was used the precipitates were more friable and amorphous. It might be expected that separation of impurities from precipitates obtained by the second method would be more complete [1].

*For communication 1, see [1].

The precipitates prepared were quantitatively transferred to the middle cell of a three-cell analyzer with cellophane membranes. Electrodialysis was carried out with cellophane membranes in an "ionic current" [2]; for this purpose the cathode cell was filled with HNO_3 solution win an initial concentration of 10^{-1} to 10^{-3} N, while the anode cell and the middle cell were filled with twice distilled water.

The experiments were continued until a minimum current was established (5-7μa), and, accordingly, a maximum voltage (2000 volt). Periodically, the solutions from the anode and cathode cells were poured into separate flasks and the impurities separated analyzed photometrically and polarographically. The contents of the impurities in the metastannic acid before and after dialysis were determined spectrographically. The results of the electrodialysis are given in Table 1.

As is evident from Table 1, removal of impurities of Fe, Cu, Pb, and Cd proceeds better from the gel of metastannic acid prepared by the second method, where the gels have a more amorphous structure and have more discrete particles than in the case of the gels obtained by means of the first method.

TABLE 2

Distribution of Activity (ThB) After Electrodialysis of Metastannic Acid Activity of the Solution Added to the Precipitate Amounted to 10,888 impulses/minute

Test solution	Volume of solution	Activity of 1 ml of solution, impulses/minute	Activity (%) of all the solution, impulses/minute	As % of the activity introduced
From the cathode cell	3	88	264	2.43
From the anode cell	10	7	70	0.64
Filtrate and wash liquor	5	20	100	0.72
After treating the ash of the anode membrane	1	58	58	0.53
After treating the ash of the cathode membrane	3	504	1512	14
Total removed from the precipitate			–	18.3
Held by the precipitate				81.7%

Nevertheless, the impurities are not removed quantitatively, and are removed to varying extents from the amorphous precipitates. The percentage content of iron is lowered one order, while the percentage content of the remaining metals (Cu, Pb, and Cd) are lowered to less than one half of an order.

As for precipitates of metastannic acid prepared by the first method, the impurities indicated are hardly removed at all in these cases. Thus, the possibility of effecting a quantitative removal of metal impurities from precipitates dispersed in water, depends, on the one hand, on the chemical nature of the dispersed material and the impurities themselves, and also, apparently, on the nature of the bond between the impurity and the particles of the dialyzed material [1].

During work with trace amounts of impurity, an aliquot of tin sulfate (0.3616 g) was dissolved in 5 ml of HCl. To this solution was added 1 ml of a soltuion of the nitrate of active lead ThB (without a carrier) •; after oxidation of divalent tin with iodine solution, the quadrivalent tin was precipitated with concentrated ammonia.

•We should like to thank G. N. Bilimovich for preparing the ThB used. The absolute amount of ThB introduced into the metastannic acid corresponded to 10^{-17} g. atom.

The solution, plus the deposited precipitate of tin was heated to the boil, and, after removing the mother liquor, the precipitate was centrifuged and washed three times with water. Filtrate and wash liquors were combined in one flask and the whole evaporated to a small accurately measured volume; this volume of solution was used for determining the activity of the material not trapped by the metastannic acid.

The precipitates were subjected to electrodialysis in an "ion current," the cathode cell being filled with a solution of HNO_3 with an initial concentration of 0.01 N; electrodialysis was carried on until a minimum current value was established (5-7 μa), and, accordingly, a maximum voltage.

During the electrodialysis process the solutions were poured out of the electrode cells into separate flasks and the cells then filled up again : the anode cell with twice-distilled water, and the cathode cell with a solution of 0.001 N HNO_3, while towards the end of the test it was filled with twice-distilled water.

All the solutions which were poured out of the electrode cells were evaporated on a water bath to small, accurately known volumes which were then used for determining the activity contained in them.

The ash of the anode and cathode membranes was treated with a small amount of concentrated nitric acid, and the solutions obtained used also for activity measurements.

The distribution of activity after electrodialysis in the anode and cathode solutions, and also in the ash of the membranes (anode and cathode is given in Table 2. It is clear from this table that unweighable amounts of impurities are hardly removed at all from precipitates of metatannic acid.

Similar results were also obtained on introducing activity antimony into metastannic acid precipitates.

Active antimony was introduced into a solution of $SnCl_2$ obtained by dissolving 1 mg of metallic tin in concentrated HCl, with subsequent addition of hydrogen peroxide, and precipitation of metastannic acid by means of concentrated ammonia solution. Excess of the electrolytes introduced were removed by electrodialysis. The precipitate of metastannic acid purified from excess electrolytes was subjected to electrodialysis in an ion current, for which purpose 0.1 N HCl in 2 ml portions was added four times into the cathode cell.

Solutions from the anode and cathode cells were periodically poured out and replaced by twice-distilled water; the collected solutions were concentrated by evaporation and their specific activity in impulses / minute determined. In the course of this work it was established that antimony hardly passes at all into the side cells as a result of electrodialysis. It was absent in the solution above the precipitate of metastannic acid in the middle cell and in the membrane material (the membranes were ashed before carrying aout activity measurements).

On the basis of the work carried out it can be concluded that trace amounts of lead and antimony cannot be removed at all from metastannic acid by means of electrodialysis.

SUMMARY

By subjecting metastannic acid with an initial concentration of Fe, Cu, Pb, and Cd of 10^{-1}% to electrodialysis, the content of these impurities can be reduced by 0.5 - 1 order. Traces of ThB and Sb^{125} cannot be removed from metastannic acid by means of electrodialysis.

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CHROMATOGRAPHIC SEPARATION OF AROMATIC CARBONYL COMPOUNDS

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The chromatographic method which has been used for separating the most diverse classes of compounds (sugars, amines, acids, amino- and ketoacids, carbohydrates alcohols, phenols, hydrocarbons, aldehydes, ketones, etc) and which has been used on a wide scale in recent years, makes it possible to solve a number of difficult analytical problems which often cannot be solved by ordinary chemical methods.

There are two paper chromatographic methods which differ from each other in principle, these are: adsorption and partition chromatography. Resolution of a mixture during adsorption chromatography is based on differences in the absorbability of the components of the mixtures on the absorbent (cellulose, acetylcellulose,etc), and depends both on the properties of the sorbent and on the choice of a suitable solvent. Separation of mixtures by means of partition chromatography is determined by differences in the partition coefficients of the components between two immiscible phases, one of which is located in the pores of the sorbent—the stationary phase —, while the second is the mobile phase. Hydrophilic materials (silica gel, cellulose, and starch) are widely used as the aqueous adsorbent. Various organic solvents usually serve as the mobile phase. The efficiency of partition chromatography is determined by the correct choice of the mobile and stationary phases ensuring the maximum possible difference in the partition coefficients of the mixture between the two phases.

Our problem was to develop a technique for the chromatographic separation of a complex mixture of aromatic carbonyl compounds formed during the oxidation of diphenylethane (benzyl, desoxybenzoin, benzoin, benzaldehyde, and phenylacetaldehyde).

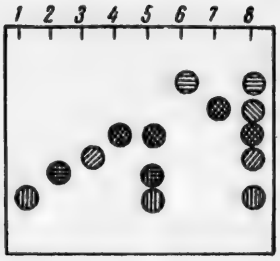
There is a large amount of published work on the chromatographic separation of carbonyl compounds of various classes. There is, however, as yet, no published information on the separation of the mixture we are interested in.

Some of the articles give some information on the possibility of separating carbonyl compounds without having to resort to making other compounds from them first [1-2], nevertheless, in most cases, derivatives of the carbonyl compounds are used. Some aldehydes and ketones can be separated in the form of their Girard derivatives [3]. These derivatives are readily soluble in water and in organic solvents. In this case the system water (adsorbed by cellulose) — organic solvent is used. Using this method, for example, 5-hydroxy-methyl-2-furfuraldehyde, 2-furfuraldehyde, and 5-methyl-2-furfuraldehyde ; salicylaldehyde, and 4-hydroxy-3-methoxy-benzaldehyde [4] have been separated.

The most widely used and the most convenient method is the separation of carbonyl compounds as their 2,4-dinitrophenylhydrazones. Both adsorption and partition chromatographic techniques can be adopted when these derivatives are used.

Separation of the 2,4-dinitrophenylhydrazones can only be achieved with difficulty on normal chromatographic paper [5] because of the hydrophilic character of cellulose. In order to get good results it is necessary to give the paper a hydrophobic character, this is carried out by esterifying the cellulose with acid anhydrides (acetic, benzoic, butyric, tartaric anhydrides, etc) [6-7].

The lower aliphatic aldehydes and ketones can also be separated on paper impregnated with sodium silicate [8].



A chromatogram of the 2,4-dinitrophenylhydrazones of the aromatic carbonyl compounds, and of their mixture:
1) Benzoin; 2) benzaldehyde; 3) phenylacetaldehyde; 4) benzyl; 5) a mixture of benzoin, benzaldehyde, and benzyl; 6) 2,4-dinitrophenylhydrazine; 7) desoxybenzoin; 8) a mixture of benzoin, phenylacetaldehyde, benzyl, desoxybenzoin, and 2,4-dinitrophenylhydrazine.

The system most often used in the practice of partition chromatography is the system water-organic solvent, nevertheless, for the separation of carbonyl compounds such sustems have a very limited application; they are used only for the separation of hydroxyaldehydes and hydroxyketones, and the 2,4-dinitrophenylhydrazones of keto acids [9-14]. Separation of the 2,4-dinitrophenylhydrazones of aliphatic aldehydes and ketones is achieved by partition between two organic solvents [15-21]. In attempting to use partition chromatography for our system we tried out almost all the solvents suggested in the literature (petroleum ether, CCl_4, benzene, alcohol, ethyl ether, $CHCl_3$, dimethylformamide, heptane, etc.). In most cases, after developing the chromatograms, continuous bands, with only a small intensification of color on individual parts, were obtained on the paper. When certain systems were used (diethyl ether and petroleum ether) diffuse spots were obtained, nevertheless, even in these cases, despite differences in the R_f values, we were unable to separate the hydrazones. Attempts to use adsorption chromatography on acetylated paper also proved unsuccessful – compact zones were obtained, but without sufficient differences in the R_f values.

A clear cut separation of the hydrazones of the aromatic carbonyl compounds was only obtained on using a combination of both chromatographic methods. Of the large number of systems tested the best one proved to be a system consisting of acetylated paper (adsorbent) impregnated with n-octyl alcohol (stationary phase) – and a mixture of hexane, toluene, and acetic acid in the proportions of 6:1:3 by volume (mobile phase).

The adsorption properties of acetylcellulose are of considerable importance for obtaining good results. In order to get uniform acetylation of the paper according to a method described previously, we used a thin spiral of teflon on which was wound a sheet of paper. Adoption of this technique prevented the sheets from sticking and the paper obtained was uniform along its whole surface. When the acetylating mixture contained even the smallest amounts of undissolved sulfuric acid, which was used as the esterification catalyst, the paper obtained was not suitable for the work, since it was brittle and unstable. Accordingly, it is essential to remove the layer of H_2SO_4 as carefully as possible from the acetylating mixture.

In order to develop this technique of chromatographic separation, synthetic mixtures were made up from carefully purified carbonyl compounds. Benzyl and benzoin (commercial) were recrystallized twice from ethanol and had melting points of 95° for benzyl and 133° for benzoin (published data 95° and 133.7°, respectively).

Phenylacetaldehyde and benzaldehyde (commercial) were distilled, the fraction boiling at 193-194° being chosen for phenylacetaldehyde and that boiling at 178-179° for benzaldehyde. The boiling points of the pure materials according to published data are 194° and 179.5°. Desoxybenzoin was prepared by the reduction of benzoin. The temperature of the material thus prepared agreed with the published value (59°).

Dinitrophenylhydrazones were prepared by the interaction of 2,4-dinitrophenylhydrazine with the corresponding compound in a weakly acid methanol solution [22]. This solution was chromatographed immediately without any procedures involving deposition of a precipitate. This speeds up and simplifies the analysis considerably. Excess 2,4-dinitrophenylhydrazine as we have shown, does not interfere with the chromatographic separation of the hydrazones, since on developing the chromatograms, this material gives its own characteristic zone which does not overlap the zones of any of the hydrazones (it is higher than all the other zones). The solution containing the 2,4-dinitrophenylhydrazones was placed on a piece of acetylated paper 120-300 mm, soaked beforehand with a 5% solution of n-octyl alcohol in CH_3OH and dried in air for 30-45 minutes. Careful drying is essential for complete removal of CH_3OH, in whose presence the zones obtained for 2,4-dinitrophenylhydrazones are less compact. The paper was then placed in a cylinder with a volume of about 2 liter, on the bottom of which was poured

30-40 ml of a mixture of hexane, toluene, and acetic acid. Under these conditions, a complete run could be carried out in 4-4.5 hours. A typical chromatogram for a mixture of the 2,4-dinitrophenylhydrazones of benzyl, desoxybenzoin, benzoin, benzaldehyde, and phenylacetaldehyde, obtained by this technique, is shown in the diagram. The yellow spots of the hydrazones, after spraying with alcoholic alkali, acquire colors which are characteristic of each carbonyl compound, the colors ranging from yellow-brown to lilac (Table 1).

TABLE 1

Test compound	R_f	Color of the spot after spraying with alcoholic alkali
2,4-Dinitrophenylhydrazine	0.76	Dirty-black
Hydrazones		
Benzoin	0.34	Yellow-brown
Benzaldehyde	0.45	Brown
Phenylacetaldehyde	0.53	Dark-brown
Benzyl	0.58	Lilac
Desoxybenzoin	0.67	Dark-brown

TABLE 2

Test compound	Initial concentration	Amount of solution taken, ml		Contraction found
		for the analysis	for the chromatogram	
Benzaldehyde	5,48 mg in 10 ml	0,3	0,4	5,94 mg in 10 ml
Benzyl	4,52 mg in 10ml	0,1	0,4	4,5 mg in 10 ml
Benzoin	4,8 mg in 10 ml	0,1	0,4	4, mg in 10 ml
Desoxybenzoin	2 mg in 10 ml	0,1	0,4	1,98mg in 10 ml

Table 1 also contains the calculated R_f values for the corresponding hydrazones. The R_f values were determined from the rates at which the solvent front and the zones moved.

These results show that it is possible to separate and identify all the carbonyl compounds formed during the oxidation of diphenylethane by a simple and convenient method.

The method developed can also be used for the separate quantitative determination of the carbonyl compounds indicated. The amount of hydrazone which can be determined is limited on the one hand, by the sensitivity of the method (10^{-7} M), and on the other hand by the solubility of the hydrazone in methanol ($2 \cdot 10^{-5}$ M in 2 ml of CH_3OH in the case of benzaldehyde, which gives the less soluble hydrazone). Accordingly, about 100 γ of the mixture of hydrazones was placed on the paper in the form of 5-8 mm wide bands. After the chromatograms had been allowed to run, each band was extracted separately with alcoholic alkali and the optical density of the solutions thus obtained measured on a FÉK-M photoelectric colorimeter. A curve showing the relation between the optical density of the solution, and the concentration of the hydrazone of the corresponding carbonyl compound, was constructed beforehand.

Table 2 illustrates the results obtained during the quantitative chromatographic separation of a synthetic mixture of benzyl, benzoin, and benzaldehyde.

In conclusion the author would like to thank N. M. Emanuel and E. A. Blyumberg for their valuable advice during the course of this work.

SUMMARY

A chromatographic method has been developed for the separation and quantitative determination of aromatic carbonyl compounds as their 2,4-dinitrophenylhydrazones. The determination is carried out on acetylated paper impregnated with n-octyl alcohol. The mobile solvent is a mixture of hexane, toluene, and acetic acid (6:1:3 by volume). The method has been used for separating a mixture of benzaldehyde, phenylacetaldehyde, benzoin, desoxybenzoin, and benzyl.

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POLAROGRAPHIC ANALYSIS OF THE LIQUID PRODUCTS OBTAINED DURING THE NITRATION OF ALKANES WITH NITROGEN DIOXIDE

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Vapor-phase nitration of alkanes (C_1-C_3) by means of nitrogen dioxide leads to the formation of a mixture of products, the quantitative analysis of which presents considerable difficulties. In such mixtures, in various experiments, the following compounds have been shown to occur: nitroparaffins, alkylnitrites, alkylnitrates, aldehydes, alcohols, alkanes, alkenes, carbon monoxide and dioxide, nitrogen oxides, and water [1-5]. Of these, nitrogen oxides, carbon oxides, and the hydrocarbons can be determined by the usual chemical or chromatographic methods. For this purpose, it is only necessary to shake the mixture with water, to remove from it the liquid reaction products (nitroparaffins, alkylnitrites and alkylnitrates, aldehydes, and alcohols) and the residue of NO_2. Analysis of the liquid products in each others presence cannot be, as yet, regarded as developed sufficiently, and this strongly impedes the development of studies of the nitration reaction.

Analysis of Liquid Nitration Products in the Absence of NO_2

An examination of the results given in Table 1 leads to the conclusion that the polarographic technique would appear to be a promising method for the analysis of such mixtures.

TABLE 1

Half-Wave Potentials ($\pi_{1/2}$) Relative to the Saturated Calomel Electrode (S.C.E.)

Compound	Half-wave potential, volt		
	Acid medium	Neutral medium (pH 7)	Alkaline medium (pH 12)
RNO_2* [1]	−0.6	−0.85	−1.0
RONO [2]	hydrolyzes	−	−0.65
$RONO_2$ [3]	−	−0.70	−0.65
HCHO [4]	−	−1.41	−1.66
CH_3CHO [5]	−	−1.63	−1.89

*$\pi_{1/2}$ does not depend on R.

In alkaline media the half-wave potentials of each material given in Table 1 differ sufficiently from each other in value to ensure their separate polarographic determination. Only the alkylnitrites and alkylnitrates are exceptions. Nevertheless, even in these cases, a combination of the spectrophotometric determination of alkylnitrite, with the polarographic determination of total alkylnitrites and alkylnitrates, makes it possible to determine each of them. [6].

The wave height for the reduction of alkylnitrites a and alkylnitrates is almost independent of the pH of the medium in the range 8 to 13 (Fig. 1). * In the same way the wave height of acetaldehyde also remains unchanged for pH changes from 10.5 to 12.5. The reduction wave of formaldehyde has a clearly defined maximum at pH 12.5, when the pH is changed from 7 to 13. Accordingly, formaldehyde in an alkaline medium must be determined

*Polarograms were taken on a "Geolrazvedka" polarograph, 1954 model. The capillary characteristics were $m^{2/3} t^{1/6} = 2.86$ mg $^{2/3}$ sec $^{1/2}$. 1 mm wave-height corresponds to $4.4 \cdot 10^{-9}$ amp. at maximum sensitivity. pH was measured on a LP-5 potentiometer using a glass electrode. Corrections for the readings of the glass electrode in the alkaline region were not made here or below.

at an accurately controlled pH corresponding to the point at which the maximum wave height is obtained. Finally, in the case of the nitroparaffins the wave height is a maximum and is constant at pH 2-7.

Thus, it can be suggested that an analysis of a mixture of the liquid nitration products of alkanes should be carried out both in alkaline and in neutral solutions; in the first medium, alkylnitrites, alkylnitrates, and aldehydes are determined, while in the second the nitroparaffins are determined. It was found, however, that the polarographic analysis of such a mixture is complicated by the capacity of the nitroparaffins to give two reduction waves not one. Petru [7] was the first to observe this phenomenon when taking polarograms of nitroethane in a Britton-Robinson buffer (pH- 1.81-11.98). Under these conditions one wave was obtained with $\pi_{1/2}$ = -0.7 volt, and a second wave (half the size) with $\pi_{1/2}$ = -1.5 volt. We found that during the polarographic reduction of nitromethane in a solution of LiCl (pH 5-6) only one wave with π = -0.85 volt was always obtained. In solutions of NaH_2PO_4 - NaOH or NaH_2PO_4 LiOH (pH 5-7), however, sometimes, there appeared two waves with $\pi_{1/2}$ = -0.85 volt and with $\pi_{1/2}$ = -1.6 to -1.8 volts, respectively. In alkaline solutions (0.2 M LiOH) of nitromethane, the second wave also appears in those cases where the solution is kept for some time before taking polarograms. Under these conditions, the higher the nitromethane concentration, the sooner the second wave appears. The height of the first wave for nitromethane is independent of the time for which the solution is kept before taking polarograms, accordingly, any quantitative determinations of the nitroparaffins should be based only on the height of the first wave. However, under these conditions, determination of formaldehyde becomes difficult, because the height of the second wave of the nitroparaffin which coincides with respect to its reduction potential with the reduction potential of formaldehyde, is subjected to sharp changes which occur for some reasons hitherto unknown.

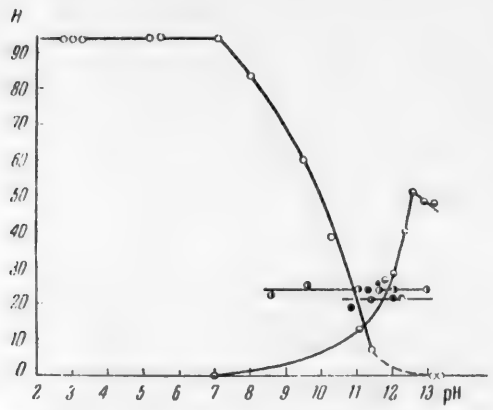

Fig. 1. Relation between wave-height and pH in unbuffered solutions (s = 1:100). o) 0.001 M solution of CH_3NO_2 (determined for a 0.00031 M solution) at 20°, supporting electrolyte 0.1 M LiOH + HNO_2; O) 0.005 M HCHO solution (determined for 0.0077 M solution) at 25°, supporting electrolyte 0.1 M LiOH + HNO_2; O) 0.001 M solution of CH_3CHO (determined for 0.01 M solution), 25°, supporting electrolyte 0.1 M LiOH + 0.1 M LiCl; O) 0.001 M solution of C_2H_5ONO (determined for 0.0038-0.0058 M solution), 25°, supporting electrolyte 0.1 M LiOH + LiCl.

To avoid the phenomenon of two waves for nitroparaffins, at least for long enough to take polarograms, it is sufficient to store the solutions at 0°.

All the same, during the polarographic analysis of a mixture of aqueous solutions of nitromethane, ethylnitrite, acetaldehyde, and formaldehyde, the results obtained were not satisfactory. The negative error obtained during the quantitative determination of alkylnitrites and aldehydes was very large, particularly in the case of the aldehydes (up to 50%). It was thought that one of the sources of error is the instability of some of the test materials in neutral or alkaline solutions at room temperature.

In checking this last assumption it was found that solutions of nitromethane, acetaldehyde, and formaldehyde (0.001- 0.03 M solutions) in water were stable for at least several months, while when dissolved in 0.1 N LiCl and in a neutral buffer of 0.2 M NaOH + 0.2 M NaH_2PO_4 they were stable for not less than a few hours. In a solution of 0.2 M LiOH the wave height for nitromethane (0.015 M) with $\pi_{1/2}$ = - 0.85 volt does not change in the course of 15 hours, while the wave height for formaldehyde (0.01 M) does not change in the course of 48 hours; the wave height for acetaldehyde, however, changes by 10% in 1.5 hours. Ethylnitrite hydrolyzes slowly in neutral solutions (H_2O, 0.1 M LiCl), nevertheless, its 0.005 M solution in 0.2 M LiOH is stable for one hour. Thus, the negative error obtained in the results for the analysis of a mixture at room temperature, cannot be explained by any interaction between the test materials and the components of the supporting electrolyte.

Another possible reason for the negative error is the interaction of these materials with each other in solution at room temperature; for example, it is well known that nitroparaffins react fairly readily with aldehydes to form nitroalcohols. In this connection therefore, solutions of binary mixtures of nitromethane and formaldehyde in 0.2 M LiOH were examined polarographically at room temperature, and the wave height for formaldehyde measured after certain time intervals. At 20° there is a fairly rapid decrease in formaldehyde concentration (Table 2) which can naturally be ascribed to its reaction with nitromethane. It was found, however, that this drop in the wave height for formaldehyde in alkaline solution is not accompanied by a drop in the wave-height for nitromethane; this last fact was established by measuring the wave height at $\pi_{1/2}$ = -0.85 volt in neutral solutions prepared by mixing alkaline solutions of formaldehyde, stored for a certain time, with 0.2 M NaH_2PO_4 solution. The fact that the wave height for nitromethane remains constant while that of the formaldehyde drops at the same time (when they are present together) may, presumably, be explained on the grounds that not only the shape and potentials of the nitroparaffin and nitroalcohol coincide (this has been observed by Seagers and Elving [8]) but also the height of the reduction wave.

TABLE 2

Change of the Height of the Reduction Wave for Formaldehyde with Time in a Solution which is 0.0006 M with respect to Formaldehyde. 0.002 M with respect to CH_3NO_2 and 0.13 M with respect to LiOH

Temperature °C	Time after solutions have been made, minutes	Wave-height, mm	Sensitivity (s)	Temperature °C	Time after solutions have been made, minutes	Wave-height, mm	Sensitivity (s)
20	0	56	1:100	0	0	34,5	1:30
20	13	47	1:100	0	18	34,5	1:30
20	31	38	1:100	0	48	35	1:30
20	42	35	1:100	0	148	27	1:30
20	68	27	1:100				

It follows from the results given in Table 2, that the reaction between the aldehyde and nitroparaffin can be slowed down appreciably by storing their alkaline solution at 0°.

A General Method for the Analysis of Liquid Products in the Absence of NO_2

On the basis of what has been said above the following experimental procedure can be adopted for the analysis of the products obtained during the vapor phase nitration of alkanes, in the absence of NO_2. Nitration itself was carried out under static conditions, where the initial pressure of alkane did not exceed 200 mg Hg (1.5- 1.7 millimole). At a chosen moment when all the NO_2 had already been transformed, the reaction mixture was withdrawn from the reactor into an evacuated trap cooled with liquid nitrogen. 20 ml of 0.2 M LiOH, or 20 ml of a buffer solution of 0.2 M NaOH + 0.2 M NaH_2PO_4 with a pH of 6-7, was then added to the trap before its contents had frozen; on adding this solution it partially froze on the trap walls during the first moment of addition. As the solution melted the trap was shaken. After the liquid products had dissolved the nitrogen oxide was removed from the trap by gaseous nitrogen at a temperature not greater than 0°. Formaldehyde and acetaldehyde were determined in 0.2 M LiOH at 0°. In calculating the formaldehyde concentration the pH was taken into account, the relation between wave height and pH having been established beforehand. Total alkylnitrites and alkylnitrates * — if present * * — can be determined in this same solution. Total nitroparaffins were determined in a buffer solution of 0.2 M NaOH (or LiOH + 0.2 M NaH_2PO_4) with a pH of 6-7 at 20°. The solution was obtained either by mixing a solution of the phosphate with part of the alkaline solution of the reaction products, prepared for determination of the aldehydes and alkylnitrites, or, by dissolving the reaction products directly in the buffer solution. In the first instance, the solution should be kept at room temperature for 1.5 hours before taking polarograms,

* The alkylnitrites were also determined on a SF-4 spectrophotometer.

* * We did not find alkylnitrites and alkylnitrates during the thermal nitration of alkanes under the conditions we chose.

polarograms, in order to allow the aci-form of the nitroparaffin to change over completely into the nitro-form which is necessary for polarographic measurements. This analytical variant has been checked on synthetic mixtures and is applicable to the analysis of the liquid products obtained during the nitration of propane and methane under static conditons. In Tables 3 and 4, and in Fig. 2. are shown the analytical results for synthetic mixtures. These mixtures were prepared from aqueous solutions of the components (apart from C_2H_5ONO, which was dissolved in 0.2 M LiOH at 0°).

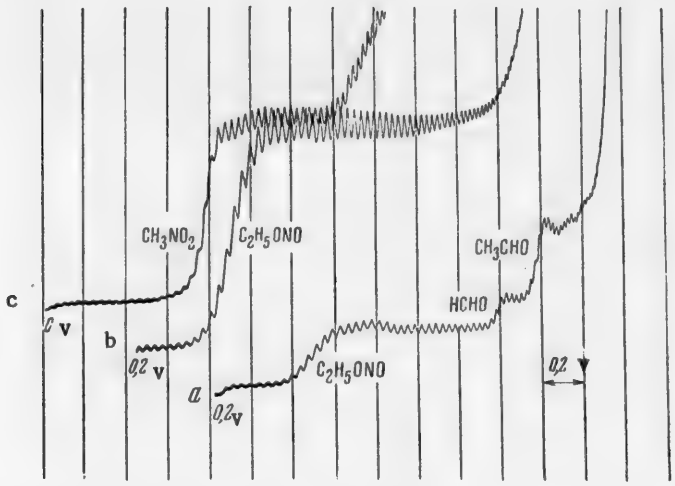

Fig. 2. Polarograms of synthetic mixtures.
a) Ethylnitrite, formaldehyde, and acetaldehyde in 0.2 M LiOH the concentrations of the components were: C_2H_5ONO-0.0063 M, HCHO-0.0120 M, CH_3CHO- 0.0027 M, CH_3NO_2-0.0056 M; s = = 1:200; 0°; pH 12.5; b) 0.0102 M ethylnitrite in a control solution of 0.2 M LiOH; s = 1:200; 0°; pH 12.5; c) nitromethane in a mixture of 1 ml of solution a) and 5 ml of a solution of 0.2 M NaH_2PO_4: = s = 1:200; 0°; pH 6.3.

TABLE 3

Polarographic Analysis of Synthetic Mixtures in the Absence of NO_2

CH_3CHO, m/liter		HCHO, m/liter		C_2H_5ONO, m/liter		CH_3NO_2, m/liter	
taken	found	taken	found	taken	found	taken	found
0,00034	0,00029	0,0020	0,0024	0,0055	0,0077	0,0070	0,0065
0,0027	0,0024	0,0120	0,0120	—	0,0018	0,0056	0,0055
0,0027	0,0024	0,0120	0,0120	0,00630	0,00567	0,0056	0,0056

The Analysis of Liquid Nitration Products in the Presence of NO_2

Additional difficulties arise when some of the nitrogen oxide which has not reacted is present in the reaction products. These arise as a result of two factors: 1) the interaction of nitrous acid, formed during the dissolution of nitrogen dioxide in water, with nitroparaffin to form nitrolic acids, and 2) the shift of the reduction potentials of Na^+ and Li^+ toward more negative values in the presence of NO_2^- and NO_3^- anions, which arise as the result of the dissolution of nitrogen dioxide in water; this renders polarographic determination of aldehydes difficult, and, sometimes impossible.

TABLE 4

Effect of the Time for which the Mixtures are Kept on Wave Height (sensitivity (s) 1:200)

Test material and concentration, mole/liter	Electrolyte	Temperature	Time, minutes (t)				
			0	5	33	50	75
			Wave-height, mm				
CH_3CHO (0,0027)	0,2 *M* LiOH	0°	27*	24	21	19	16
HCHO (0,012)	0,2 " "	"	8*	8	8	8	8
C_2H_5ONO (0,00630)	0,2 " "	"	16,2*	14,5	14	14	14
CH_3NO_2 (0,0056)	0,2 *M* NaOH + 0,2 *M* NaH_2PO_4 pH 6—7	20°	43*	—	—	—	43

*Calculated on the basis of the wave-height in the one component control solution; the time when the mixture is made up is taken as t = 0.

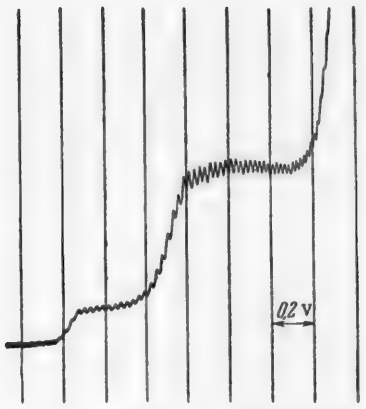

Fig. 3. Polarogram of methylnitrolic acid obtained by dissolving a mixture of the vapors of 0.3 millimole of NO_2 and 0.085 millimole of CH_3NO_2 in 20 ml of 0.2 M LiOH; s = 1:200; 0°; pH 12.4.
The first abscissa at 0.4 volt.

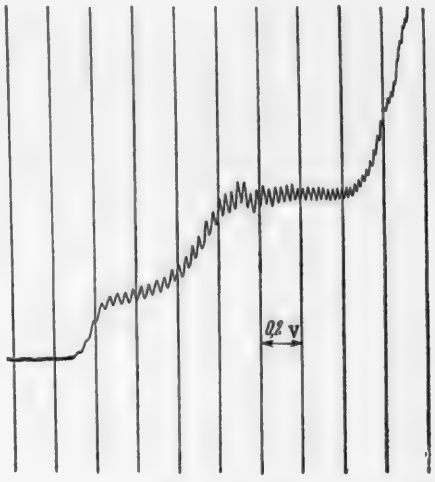

Fig. 4. Polarogram of methylnitrolic acid synthesized by Gatterman's method, and dissolved in 0.2 M LiOH; s = 1:500; 20°; pH 12.5.
First abscissa at 0.2 volt.

Attempts to remove nitrogen dioxide directly from a partially reacted mixture of RH and NO_2 which is to be analyzed, without changing the composition of the remainder, proved unsuccessful. Accordingly, the difficulties indicated had to be overcome by another method.

a) Polarographic Analysis of a Mixture of Nitroparaffin and NO_2. On dissolving a mixture of a nitroparaffin and nitrogen dioxide in a large excess of an aqueous alkaline electrolyte (under the experimental conditions) formation of free nitrous acid cannot be avoided. The latter slowly reacts with the nitroparaffin to form nitrolic acids, which leads to a decrease in the nitroparaffin concentration. We were unable to avoid formation of nitrolic acids by lowering the temperature at which the components were dissolved, or by cutting down the time taken to dissolve the components by mixing (down to one second). In Fig. 3 is shown the polarogram of an alkaline solution obtained by pouring 20 ml of 0.2 M LiOH into a mixture of 0.085 millimole of nitromethane

and 0.3 millimole of nitrogen dioxide frozen at -78°. Two reduction waves can be observed on the polarogram, one with $\pi_{1/2}$ = -0.6 volt and a second with $\pi_{1/2}$ =-1.1 volt.* Similar waves were obtained during the reduction of alkaline (0.2 M LiOH) solutions of methylnitrolic acid synthesized either by Gatterman's method [9] (Fig. 5) or by acidification of a mixture of aqueous solutions of nitromethane and $NaNO_2$ (see Fig. 5). This confirms the formation of a nitrolic acid on dissolving a frozen (-78°) mixture of nitromethane and NO_2 in 0.2 M LiOH, presumably, as the result of the appearance of free acid in various parts of the mixture. In this case, from 10 to 40 % of the original nitromethane is converted into a nitrolic acid.

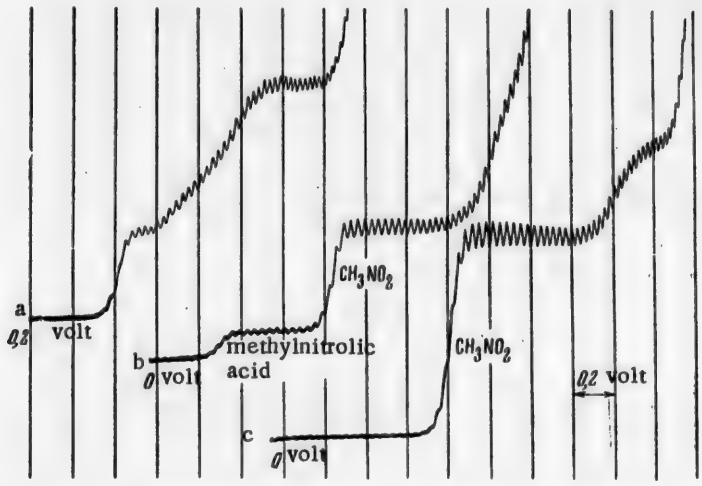

Fig. 5. Polarogram of methylnitrolic acid in alkaline a), and neutral solutions b), obtained by acidification of a mixture of CH_3NO_2 and $NaNO_2$.
a) 2 ml of 0.567 M CH_3NO_2 + 20 ml of 0.02 M $NaNO_2$. pH 7 $\xrightarrow{2\text{ M }HNO_3}$, pH 2.1, $\xrightarrow{1.2\text{ M NaOH}}$ pH 12.1, s = 1 : 100, 20°; b) 2 ml of solution a) + 7 ml of 0.2 M NaH_2PO_4; s = 1:200; pH 7.1; final concentrations of CH_3NO_2 calculated from the amount taken in experiment a) = 0.0041 mole/liter; in experiment b) 0.0091 mole/liter; c) polarogram of the control solution of nitromethane in a mixture of 0.2 M NaOH + 0.2 M NaH_2PO_4; [CH_3NO_2] is equal to 0.0014 M; s= 1:200; 20°; pH 7. X – methylnitrolic acid

Formation of nitrolic acids can be avoided by directly dissolving the mixture of the products obtained during the nitration of alkanes in a neutral phosphate buffer. This is evident from a consideration of the polarograms shown in Fig. 6 and which were obtained as follows; Three nitrations of propane were carried out under similar conditions (mixture of $4C_3H_8 + NO_2$; T = 250°; $P_{initial}$ = 312 mm Hg; time for completion of reaction 22 minutes, corresponding to complete usage of the nitrogen dioxide). The products of the first nitration (Fig. 6.b) were dissolved in a buffer solution (0.2 M NaH_2PO_4 + 0.2 M NaOH; pH 7); while to the products of the second and third nitration was added 2 millimole of nitrogen dioxide. The products of the second nitration, with the added nitrogen dioxide, was dissolved first in 0.2 M LiOH, and then part of the alkaline solution was mixed with 0.2 M NaH_2PO_4 solution (Fig. 6 a). The products of the third nitration together with the added nitrogen dioxide were dissolved in a phosphate buffer (Fig. 6 c). In addition, for purposes of comparison, polarograms were taken of known methylnitrolic acid dissolved in a phosphate buffer with a pH of 6. When this was done a reduction wave

*Polarographic waves are not observed in separate alkaline solutions of nitromethane and nitrogen dioxide.

with $\pi_{1/2}$ = -0.25 - 0.3 volt (see Fig. 7) was found. It is clear from this, that of the three polarograms in Fig. 6, only in the case of 6 a is there a wave for nitrolic acid ($\pi_{1/2}$ = -0.3 volt), in the case of 6 c it is absent.* It is obvious that on dissolving the nitration products in a neutral phosphate buffer there is not even a short-time formation of free nitrous acid.

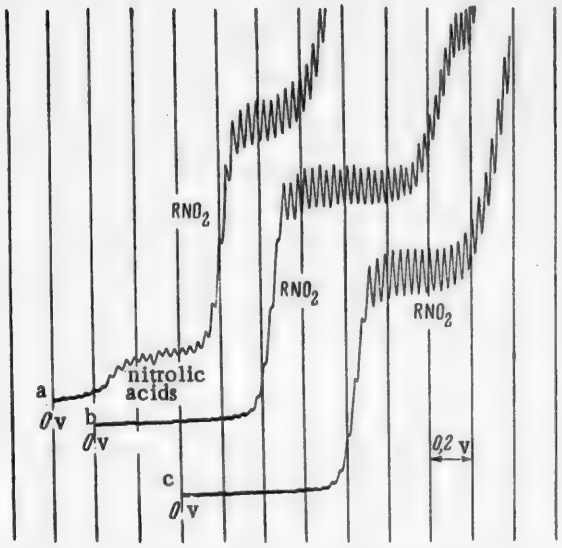

Fig. 6. Polarograms for solutions of mixtures of the reaction products with and with and without addition of NO_2; 20°; [RNO_2] determined on the basis of the wave with $\pi_{1/2}$ = 0.85 volt. a) To the reaction products was added 2 millimole of NO_2 followed by 20 ml of 0.2 M LiOH. Part of this solution was mixed with 0.2 M NaH_2PO_4 in the proportion of 2 : 4; s = 1: 200; pH 6.2 0.068 millimole of RNO_2 found. b) The reaction products were dissolved in 50 ml of a mixture of 0.2 M LiOH + 0.2 M NaH_2PO_4; s = 1: 500; pH 6.4; 0.135 millimole of RNO_2 found.

b) Determination of Alkylnitrities and Alkylnitrates in the Presence of NO_2. As indicated already, it is difficult to avoid formation of nitrolic acids on dissolving the nitration products in alkaline solution when they contain nitroparaffins and NO_2 (or HNO_2). This makes it very difficult to carry out a polarographic determination of alkylnitrites and alkylnitrates, since the reduction wave of the latter coincides with the reduction wave of nitrolic acid ($\pi_{1/2}$ = -0.65 volt in alkaline media). In order to determine total RONO and $RONO_2$ in the presence of nitrolic acids we made use of the fact that nitrolic acid remains in aqueous solution even when nitrogen is blown through the solution for a long time, while both RONO and $RONO_2$ are completely expelled by the nitrogen stream in 10-20 minutes at room temperature. For example, on blowing nitrogen through a) a 0.0017 M solution of C_2H_5ONO in 0.2 M LiOH (solution A), through b) an alkaline solution of methylnitrolic acid prepared by successively pouring together 2 ml of 0.056 M CH_3NO_2, 20 ml of 0.02 M $NaNO_2$, 0.45 ml of 2 M HNO_3, and 1.6 ml of 1.2 M NaOH (solution B), and c) through a mixture of 2 ml of solution A and 7 ml of solution B, it was found that ethylnitrite was removed from solution A and from mixture of solutions A and B to the extent of 99% in the course of 10 minutes, while the concentration of methylnitrolic acid in solution B, and in a mixture of solutions A and B, remained constant for not less than 35 minutes. Thus, in order to determine total alkylnitrates in the presence of nitrolic acids and the other nitration products in 0.2 N LiOH, first of all determine the total wave height of the nitrites, nitrates, and nitrolic acids with $\pi_{1/2}$ = -0.6-0.65 volt at 0°, and then blow nitrogen through the solution at room temperature until the height of the polarographic wave indicated is constant, and finally repeat the determination at 0°. The value obtained at 0° determines the amount of nitrolic acids. The difference between the first and third determinations at 0° corresponds to the sum of the alkylnitrites and alkylnitrates.**

c) Mixtures of Aldehydes and NO_2. Since, in the presence of NO_3^- (or NO_2^-), the origin for the reduction of Li^+ is shifted toward more positive potentials, the shift being greater ther higher the concentration of these ions, then, starting at some definite NO_3^- (or NO_2^-) concentration polarographic analysis of aldehydes becomes impossible. For example, when polarograms are taken of 0.0008- 0.0018 M solutions of formaldehyde in 0.2 M LiOH, determination of formaldehyde is impossible when the concentration of NO_3^- is greater than 0.01-0.05 mole/liter. For acetaldehyde this limit is lowered 10 times (0.001-0.005 mole/liter).

*In the case of 6 b, nitrolic acid cannot be formed, since nitrogen dioxide is not present in the mixture of products.

**We used this method for determining nitrites (nitrates were absent) in the presence of nitrolic acids in the products obtained by the interaction of alkyl radicals and NO_2.

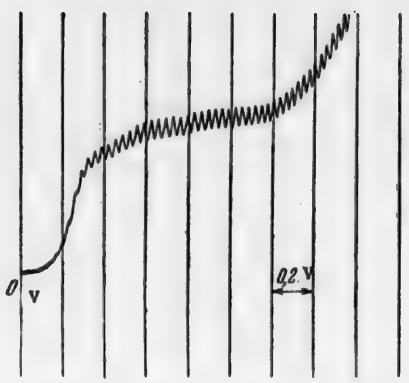

Fig. 7. Polarogram for methylnitrolic acid dissolved in a mixture of 0.2 M LiOH + 0.2 M NaH_2PO_4; s= 1:500; 20°; pH 5.6.

One way out in the case of the polarographic determination of formaldehyde would appear to be dilution of the alkaline solution so as to lower the NO_3^- (or NO_2^-) concentration. The success of such an approach is determined by the concentration of the aldehyde and of the NO_3^- (or NO_2^-) and their proportions. For the polarograph which we used, the limit is $1.5 \cdot 10^{-5}$ M formaldehyde when the determination is carried out at 25°, and $2 \cdot 10^{-4}$ M when the determination is carried out at 0° (the wave height in both cases is 2 mm for a sensitivity of 1:10).

Positive results for the determination of acetaldehyde can be obtained by preliminary removal of NO_2^- and NO_3^-, by supercooling the test alkaline solution in a vacuum.

Thus, on supercooling a 0.0002 M CH_3CHO solution, containing 0.015 mole/liter of NO_3^-, and then heating the trap with warm water for 1-2 hours, it is possible to determine 93% of the CH_3CHO (the presence of nitromethane leads to low results when the temperature of the trap is taken above 0°).

TABLE 8

Analysis of Synthetic Mixtures in the Presence of NO_2

Composition of the mixture	HCHO, m/liter		CH_3NO_2, m/liter		CH_3CHO, m/liter	
	taken	found	taken	found	taken	found
1ml 0,030 *M* HCHO; 4 ml 0,019 *M* CH_3NO_2; 0,5 ml 0,0136 *M* CH_3CHO; 14,5 ml 0,28 *M* LiOH; 0,2 m/ mm NO_2, pH 12,2	0,0015	0,0013	Not determined		Not determined	
8ml 0,030 *M* HCHO; 4ml 0,019 *M* CH_3NO_2; 4 ml 0,0136 *M* CH_3CHO; 2 m/ mm NO_2; 4 ml 1 *N* NaOH+NaH_2PO_4, pH 5,75	not determined		0,0038	0,0037	not determined	
0,5ml 0,030 *M* HCHO; 5ml 0,019 *M* CH_3NO_2 0,5 ml 0,0136 *M* CH_3CHO; 2 m/ mm NO_2; 4 ml 1 *N* LiOH; 10 ml H_2O, pH 12,4*	not determined		not determined		0,00034	0,00033

*See footnote on page 201.

d). Mixtures of Aldehydes, Nitromethane, and NO_2. Satisfactory results for the determination of acetaldehyde in the presence of nitromethane, formaldehyde, and NO_2 were obtained by the following technique. 5 ml of an aqueous solution of the aldehydes and of nitromethane, 0.2 M with respect to LiOH and prepared at 0°, was poured into a trap containing frozen nitrogen dioxide, and the whole mixed. The solution was supercooled at 0° by agitating it in the trap, cooled with liquid nitrogen, by means of a stream of nitrogen. Supercooling took about 5 hours. To the solution obtained was added at 0°, 0.5 ml of 0.1 M LiOH. Polarograms were also taken at 0°. It should be pointed out that on supercooling the alkaline solutions, a large part of the formaldehyde and nitromethane is lost (up to 90%). It is possible that nitromethane is precipitated as the salt of a nitrolic acid, which is not supercooled, while the formaldehyde forms hydrates with a low vapor pressure and is then polymerized on concentrating the solution.

The following results can be adduced as examples. In a mixture consisting of 0.125 ml of 0.0136 M CH_3CHO, 1.25 ml of 0.019 M CH_3NO_2, 0.125 ml of 0.030 M HCHO, 0.5 millimole of NO_2, 2.5 ml of H_2O, and 1 ml of 1 M NaOH (in such a mixture [CH_3CHO].= 0.00034 M) 0.00033 mole/liter of CH_3CHO was found.

General Method for the Analysis of Liquid Products in the Presence of NO_2

The analytical procedure adopted in the presence of nitrogen dioxide differs from the analytical method used in its absence in the following respects:

a) Nitroparaffins. For determination of the nitroparaffins, the nitration products should be dissolved in a buffer mixture of 0.2 M NaOH + 0.2 M NaH_2PO_4, containing an excess of NaOH such that, after diluting and neutralizing the NO_2, the pH of the solution should be 6-7. One cannot use a solution by mixing it with NaH_2PO_4, since on dissolving the LiOH, some of the nitroparaffins are converted into nitrolic acids.

b) Formaldehyde. The method remains unchanged, but as indicated already, formaldehyde cannot be determined in the presence of a large excess of NO_2.

c) Acetaldehyde. The nitration products are dissolved in 0.2 M LiOH at 0°, as indicated above. It is necessary to take LiOH in twofold excess with respect to the amount of NO_2 it is desired to neutralize. The method of supercooling at 0° in a stream of nitrogen, by the technique indicated above, is then used.

d) Alkylnitrates and Alkylnitrites are determined as described above. It must be emphasized that satisfactory results can only be obtained by taking polarograms in LiOH solution when all the manipulations are made rapidly and at a temperature not higher than 0°. It is recommended that the electrolytes be purged of oxygen by blowing nitrogen or hydrogen through them, before dissolving the reaction products in them, otherwise, during the purging process some of the reaction products will be lost.

This technique has been tried out on synthetic mixtures prepared by dissolving NO_2, frozen in a trap, in mixtures of solutions of nitromethane, acetaldehyde, and formaldehyde. One of the components was determined in each of the mixtures. The stability of the mixtures in the presence of NO_2^- and NO_3 was the same as in the absence of these anions (Table 5). The accuracy of the results obtained (Table 8) is not less than in the absence of NO_2.

As indicated above, the analytical method developed was used for the quantitative determination of the liquid products obtained by the thermal nitration of propane and methane, and by the low-temperature interaction of alkyl radicals with nitrogen dioxide. We were unable to detect any other waves on the polarograms apart from those belonging to the nitroparaffins, alkylnitrites, aldehydes, and nitrolic acids. It was also established that, on using the method developed, nitrogen oxides present in the nitration products do not give polarographic waves. The presence of the oxides only leads to the formation of nitrolic acids, and to a shift in the reduction potential of the base electrolyte.

The deviation between the results of parallel experiments did not, as a rule, exceed 10% of the values determined.

SUMMARY

A method has been developed for the quantitative polarographic analysis of mixtures of the liquid products obtained during the thermal nitration of alkanes, and during the low-temperature interaction of alkyl radicals and nitrogen dioxide; this method permits determination of total nitroparaffins, total alkylnitrites, formaldehyde, and total higher aldehydes, both in the absence and the presence of nitrogen dioxide.

Determination of formaldehyde in 0.2 M LiOH is possible as long as the NO_3^- concentration is not higher than 0.01-0.05 mole/liter.

When alkylnitrites and alkylnitrates are present together, the method gives their sum.

Polarograms of methylnitrolic acid have been obtained for the first time. In 0.2 M LiOH solution the polarogram for methylnitrolic acid consists of two waves, with $\pi_{1/2}$ = -0.6 volt and $\pi_{1/2}$ = -1.0 volt with respect to the saturated calomel electrode. Only one wave with $\pi_{1/2}$ = -0.6 volt and $\pi_{1/2}$ = -0.6 volt and $\pi_{1/2}$ = -0.25--0.3 volt is observed in a buffer solution of 0.2 M NaOH + 0.2 M NaH_2PO_4 with a pH of 5-7.

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DETERMINATION OF GOLD BY AN ELECTROMETRIC NONCOMPENSATING METHOD

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The electrometric noncompensating method for the quantitative determination of gold is based on the reduction of Au^{III} or Au^{I} by ferrous sulfate to metallic gold in acid media at room temperature. The indicator electrode used is a gold wire, or a gold-plated platinum wire, while a sulfate-copper electrode is used as the auxiliary electrode; its construction is described in a previous article [1].

Electrodes which are short-circuited through a small external ohmic resistance R are used in electrometric noncompensating titration. An indicator – a needle galvanometer or microameter is connected in series in the circuit. It was established experimentally that the value of the potential differences of the short-circuited electrodes, (gold)ϵ_k and (the auxiliary)ϵ_a, and the strength of the polarization current I depends on the value of the external resistance R and the internal resistance r in accordance with Ohm's law

$$I = (\epsilon_k - \epsilon_a) / (R + r) \qquad (1)$$

On short circuiting the electrodes through the external resistance R > 1000 ohms, the value of r remains so small that it can be disregarded in equation (1). Accordingly, the relation indicated above can be expressed by the equation

$$I = (\epsilon_k - \epsilon_a)/R \qquad (2)$$

The potential of the gold electrode in the solution being titrated is determined by the concentration of Au^{III} and the value of R. In the noncompensating method for titrating Au^{III}, electrodes which are short circuited through a resistance of about 20,000 ohms are used. The potential of the sulfate-copper electrode does not depend on the composition of the solution being titrated, it is determined only by the composition of the electrolyte in the agar gel and the value of R. Under equilibrium conditions the sulfate-copper electrode has a potential of about 0.30 volt with respect to the normal hydrogen electrode. In solutions of Au^{III} and Au^{I} a gold electrode has a potential which is always more positive than the sulfate-copper electrode, accordingly in a close electrode pair, the first operates as a cathode and the second as an anode.

Under these conditions the following reaction occurs on the cathode

$$Au^{III} + 3e \rightarrow Au^{0}.$$

Another reaction, equivalent to the above, occurs on the copper electrode under the same conditions

$$Cu^{0} \rightarrow Cu^{III} + 2e$$

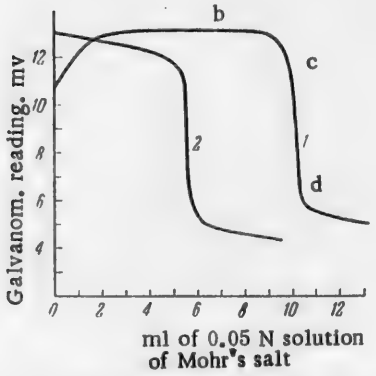
The method described below for the determination of gold was developed for the analysis of jeweller's alloys, containing silver and copper, in addition to gold.

Experimental investigations were carried out with the aim of establishing the possibility of carrying out a

direct titration of gold with a solution of Mohr's salt, without removal of nitrous acid and separation of AgCl.

Synthetic solutions were prepared from $HAuCl_4$, $CuSO_4$, $AgNO_3$, and concentrated acids. The method developed has been checked in the Sverdlovsk Inspectorate of the Assay Service of the USSR Ministry of Finance.

A sample of test alloys was dissolved in a mixture of hydrochloric and nitric acids (aqua regia). During this process the gold and copper dissolve, while silver is precipitated as AgCl. The solution also contains excess hydrochloric and nitric acids.



1) Titration curve of $HAuCl_4$ with a solution of Mohr's salt; 2) titration curve for the part of the gold remaining after precipitation of the greater part of it with Mohr's salt.

The indicator apparatus used was a needle galvanometer with a 17 millivolt scale and R_t = 260 ohms. One galvanometer division corresponded to 0.2 millivolt or 0.78 μa. The test solutions were titrated with about a 0.05 N solution of Mohr's salt in 5% H_2SO_4. The electrode pair were closed through a resistance of 20,000 ohms. The solution was agitated by rotating the beaker placed on rotating table [2] rotating at 180 revolutions/minute.

Titration Curves. During titration of gold solutions, the galvanometer does not directly measure the difference in potentials $\Delta\epsilon$ of the closed electrodes, but the polarization current I. The latter is related functionally to $\Delta\epsilon$ in accordance with Ohm's law. In our case, only the gold electrode reacts to changes in the composition of the solution, accordingly, at constant R, the value of I will be proportionally related only to the potential of the gold electrode.

The curves obtained during the noncompensating method can reflect, depending on the coordinates chosen, the change in the current, of the potential differences of the closed electrodes. The curve shown in the diagram expresses the change in the potential of the gold electode during the titration of a solution of $HAuCl_4$.

During titration of $HAuCl_4$ solutions, deposition of gold metal in the precipitate was not observed once. Over the part ab of the titration curve, the solution remained clear. Deposition of gold only occurred on the part bc and finished over the part cd. During this process, for the titration from a to b, i.e. to the beginning of the deposition of gold, 2/3 of the total amount of Mohr's salt taken altogether was used. On this basis it can be assumed that the reduction of Au^{III} to Au^0 proceeds successively in two stages:

$$Au^{III} + 2e \rightarrow Au^{I}$$
$$Au^{I} + e \rightarrow Au^{\circ}.$$

During the first stage, AuCl which is soluble in water is formed, consequently the solution remains clear.

The standard (normal) electrode potential of gold in a solution of its ions has not yet been determined accurately. According to Latimer [3] it is given by

$$\varphi^{\circ}_{Au^{I}/Au^{\circ}} = \sim 1{,}68 \quad \text{and} \quad \varphi^{\circ}_{Au^{III}/Au^{\circ}} = 1{,}50,$$

while according to Lur'e [4] it is given by

$$\varphi^{\circ}_{Au^{I}/Au^{\circ}} = 1{,}50 \quad \text{and} \quad \varphi^{\circ}_{Au^{III}/Au^{\circ}} = 1{,}29 \text{ volts on the hydrogen scale}$$

The shape of the titration curves for solutions of $HAuCl_4$ completely agrees with the ratio of the values of the electrode potentials of the gold electrode indicated above. The rise on the titration curve corresponds with an increase in the potential of the gold electrode which arises as a consequence of the appearance in the solution

of Au^{I} ions in increasing concentrations. The absence of a maximum at the point b can be explained by the small dissociation of $[AuCl_4]^-$ and AuCl (or $AuCln^{1-n}$). For the first, $K = 5 \cdot 10^{-22}$, but for the second, K is unknown.

As indicated above, during the titration of the test solutions there occurs a partial loss of the gold, as a result of its deposition on the gold cathode. The amount of this loss in grams can be found by means of the equation

$$m = IMt/zF.$$

In this equation I is the current strength in amp./second; M is the atomic weight of gold; t is the duration of an experiment in seconds; z is the charge on the gold cation; and F is the Faraday constant. By comparing equations (2) and (3) we get

$$m = \frac{(\varepsilon_k - \varepsilon_a) Mt}{RzF}.$$

From the last two equations it is clear that the extent of the loss of gold on the gold electrode will be proportional to the current of the working electrode pair, the duration of the experiment and the value of the potential of the gold electrode, and will be inversely proportional to the value of the external resistance.

In our experiments the value of I did not exceed 40 μa, while the titration lasted not more than 5 minutes. Under such conditions the amount of gold lost on the cathode during the reduction of Au^{III} to the metal amounts to

$$m = \frac{40 \cdot 10^{-6} \cdot 197 \cdot 5 \cdot 60}{3 \cdot 96500} = 8{,}5 \cdot 10^{-6} \text{ g}$$

while during the reduction of Au^{I} the amount of gold lost should be three times greater.

For many technical methods of analysis such a loss would not be particularly important, but for the analysis of gold alloys which demands especially high accuracy, the extent of this loss cannot be ignored.

During the electrometric noncompensating method of analysis the loss of gold on the cathode can be cut down as follows:

1. By increasing the external resistance R by using a more sensitive galvanometer. The use of mirror galvanometers make it possible to cut down the amount of gold lost 10-20 times;

2. By cutting down the time taken for titrating, and also by the immediate addition of a large portion of the Mohr's salt solution to the solution being titrated, with subsequent titration to the end with the same solution of Mohr's salt of the remaining small amount of gold. This technique has been used in the procedure given below for the determination of gold in jeweller's alloys.

3. The experimental error can also be reduced to a minimum by keeping the titration time a constant. Thus, by using an empirical titer, or by introducing a correction for the gold precipitated, analysis of gold alloys can be carried out with an accuracy of 0.5-to 1.0 or 0.05-0.1%.

Titration Conditions. The following facts were established in the course of some special experimental studies.

During titration of gold, Fe^{2+} cations are not oxidized by nitric acid in the presence of HCl, accordingly there is no need to remove the nitric acid from the solution after dissolving the gold.

AgCl precipitates do not interfere with titration of gold.

Copper salts not only do not interfere, but even exert a favorable effect on the shape of the titration curves; accordingly copper in the form of $CuSO_4$ is deliberately added to the solution being titrated.

Hydrochloric acid has an unfavorable effect both on the shape of the titration curves and on the amount of

Mohr's salt used up in the titration; the jump on the titration curve decreases with increasing hydrochloric acid concentration, while the amount of Mohr's salt used up increases.

Good results are obtained in the presence of orthophosphoric acid. The curves show exceptional reproducibility and have a shape which is suitable for establishing the endpoint. Chlorides, nitrates, sulfates, Cu^{2+}, and AgCl do not interfere with titration of gold in the presence of H_3PO_4.

The results of our studies made it possible to devise the following fairly simple analytical scheme; an aliquot of alloys is dissolved in concentrated aqua regia, this solution is neutralized with concentrated alkali solution, after which the solution is re-acidified with phosphoric acid, and is finally titrated with Mohr's salt.

Determination of the Expenditure of Mohr's Salt. It was pointed out above that in order to cut down the amount of gold lost on the cathode, it is expedient to add a large amount of the Mohr's salt to the solution being titrated right at the beginning, the amount added being such that some gold is left in the solution ;the gold remaining is then titrated to the end with the same solution of Mohr's salt. The Mohr's salt was standardized against pure gold.

EXPERIMENTAL PROCEDURE

An aliquot of rolled, finely cut gold alloys, of quality 583,(about 0.18 g) is weighed on an assay balance to the fifth decimal place. It is transferred to a dry 250-300 ml chemical beaker and covered with 15 ml of a mixture of HCl + HNO_3 (3:1), the beaker is covered with a watch glass and heated on a sand bath or on an open electric hotplate.

The mixture of hydrochloric and nitric acids should be prepared fresh daily from the pure concentrated acids. In such a mixture the alloy dissolves very readily without deposition of AgCl. When the acids used are not concentrated enough (sp.gr. less than 1.19 and 1.40) AgCl is deposited on the lumps of alloy and strongly hinders dissolution of the alloy.

When the alloy is being dissolved, the solution should not be shaken, otherwise solution which gets on to the walls will sputter and may overheat. Neither should the solution be evaporated to dryness. In the latter instance and in the case of overheating on the beaker walls, partial decomposition of auric to aurous chloride may occur ($AuCl_3 \rightarrow AuCl + Cl_2$).

After the alloy has dissolved and the solution has been cooled, the watch glass and the beaker walls are washed with distilled water. During this process AgCl is deposited. Washing should be carried out with the minimum amount of water.

To the acid solution is added 5.0 ml of 10% $CusO_4$ solution prepared from chemically pure $CuSO_4 \cdot 5H_2O$ free from $FeSO_4$. The solution is neutralized with 30% NaOH (or KOH) until a black precipitate forms (Ag_2O).

In order to dissolve the precipitate formed, and in order to create an acid medium, 5.0 ml of 80% H_3PO_4 free from phosphorous acid H_3PO_3 is added to the solution. The AgCl precipitate remaining does not interfere with titration of gold.

To the phosphoric acid solution is added by means of a pipet exactly 25.00 ml of approximately 0.05 N Mohr's salt solution in 5% H_2SO_4. During this stage the bulk of the gold is precipitated, the remaining gold is then titrated with the same solution of Mohr's salt to the end point. The amount of Mohr's salt used is determined from the titration curve as indicated above.

After completing the titration, the precipitate of gold and AgCl is filtered off, washed with water, and then with concentrated ammonia in order to remove the AgCl. The filter plus gold are dried and calcined in a porcelain crucible until the powdered gold sinters.

Standardization of Mohr's Salt. The Mohr's salt can be standardized either against pure gold of not less than 999.9 quality, or by means of a sample of alloy whose gold content is accurately known. During the standardization of Mohr's salt by means of pure gold or by means of a gold alloy, all the operations described above for preparing test material for analysis, as well as the titration itself are carried out exactly the same way as outlined in the above procedure. About 0.110 g of pure gold, weighed out to the fifth place, is taken.

SUMMARY

An electrometric noncompensating method has been developed for the determination of gold in jeweller's alloys by titration with a solution of Mohr's salt.

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SEPARATION OF THORIUM FROM THE RARE-EARTHS BY MEANS OF TANNIN*

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Schoeller [1] who successfully used tannin for separating tantalum and niobium, indicated that thorium is quantitatively precipitated in a neutral tartrate solution together with aluminum, iron, chromium, titanium, zirconium, vanadium, niobium, tantalum, and uranium. The rare-earths are quantitatively precipitated by tannin in the presence of excess ammonia, both in solutions containing tartaric acid and also in the absence of the latter. Information regarding the possibility of separating thorium and the rare-earths by means of tannin, is, however, nonexistent.

TABLE 1

pH Values at which Hydroxides Start of Precipitate

Cations	Anions		
	Cl^-	NO_3^-	SO_4^{2-}
Ce^{IV}		3,1[4]	
Th^{IV}	3,51[4]	3,57[4]	3,53[4]
Sc^{III}	4,90[5]		4,80—4,90[5]
Lu^{III}		6,30[6]	6,18[6]
Yb^{III}		6,30[6]	6,18[6]; 6,16[7]
Tu^{III}		6,40[6]	6,21[6]
Er^{III}		6,76[6]	6,50[6]
Gd^{III}		6,83[6]	6,75[6]
Eu^{III}		6,82[6]	6,68[6]
Sm^{III}	6,83[4]	6,92[6]; 6,83[4]	6,70[6]
Y^{III}	6,78[4]	6,95[6]; 7,39[6]	6,83[6]; 7,39[6]
Nd^{III}	7,02[4]; 7,40[7]	7,31[6], 7,02[4]	6,95[6]; 6,73[7]
Pr^{III}	7,06[4]	7,35[6]	7,17[6]; 6,98[7]
Ce^{III}	7,41[4]	7,60[6]; 8,10[6]	7,35[6]; 7,07[7]
La^{III}	8,03[7]	7,82[6], 8,35[4] 8,71[6]	7,41[6]; 7,61[7]

*This work was carried out in 1949.

Neish [2] a long time before the appearance of Schoeller's paper noted that "tannin quantitatively precipitated thorium, but does not precipitate cerium, lanthanum, and didymium." Venkataramanian, Satyanarayanamurthy, and Rao [3], in addition to other methods of separating thorium from the cerium subgroup of the rare-earths, very briefly described a method based on the precipitation of thorium by means of tannin from acetic acid solution.

The present article contains a description of another method of solving the problem of separating thorium from the cerium, as well as from the yttrium subgroup of the rare-earths, by means of tannin.

The use of tannin in analytical chemistry is based on its colloidal-chemical properties [1]. Tannin is a mixture of the esters of digallic acid and glucose, the most important of which is pentadigalloglucose—a material with a molecular weight of about 1700. Aqueous solutions of tannin, like those of many other high molecular weight polyelectrolytes, contain fairly large negatively charged particles, and possess some properties which are typical of colloidal solutions. With highly dispersed positively charged hydrosols of the hydroxides or basic salts of certain metals, tannin, under certain conditions (temperature, concentration, pH, etc.) forms adsorbed compounds which separate out of solution in the form of large flocs.

The hydroxides of the trivalent rare-earths, as a rule, are quantitatively precipitated in alkaline media.

Some of them, as is evident from Table 1, start to precipitate at a pH of 6.2. Thorium hydroxide starts to precipitate in a more acid medium at pH 3.5. The pH values indicated are almost independent of the nature of the anions present, and remain constant for dilute nitric, sulfuric, and hydrochloric acid solutions [4]. The existence of a fairly considerable difference between the pH values at which the rare-earths and thorium are precipitated, serves as a basis for their quantitative separation.

For preparing the working solutions of thorium, a preparation of thorium nitrate $Th(NO_3)_4 \cdot 4H_2O$ was used, in which the amount of rare-earths, present as impurities, did not exceed 0.1% as established by x-ray spectrochemical analysis. The starting material used for preparing solutions of the rare-earths in nitric acid, was a mixture of the oxides having the following composition according to the results of x-ray spectrographic analysis carried out by I. B. Borovskii:

CeO_2	48%	Y_2O_3	4 %
La_2O_3	23	Gd_2O_3	1,2
Pr_6O_{11}	4	Tb_4O_7	0,3
Nd_2O_3	16	Dy_2O_3	0,3
Sm_2O_3	3	PbO	0,1

The working solutions of thorium nitrate, and of the mixture of the nitrates of the rare-earths, were standardized gravimetrically by weighing the oxides obtained by calcining the hydroxides, oxalates, and dry residues obtained on evaporating their solutions to dryness.

As tests showed, tannin quantitatively precipitates thorium in approximately 0.005 N nitric or hydrochloric acid solution (Table 2 and 3).

TABLE 2

Determination of Thorium in Nitric Acid Solutions
(0.0100 g ThO_2 taken)

HNO_3, N	ThO_2 found, g	Error, g
0,004	0,0099	—0,0001
0,006	0,0097	—0,0003
0,006	0,0100	—0,0000
0,009	0,0090	—0,0010
0,009	0,0091	—0,0009
0,011	0,0091	—0,0009
0,011	0,0085	—0,0015

For complete precipitation of thorium the amount of tannin taken should be five times the weight of thorium as the dioxide, and not less than 1 g per 100 ml of solution. The presence of ammonium chloride or nitrate in small amounts up to 1 g per 100 ml of solution makes it possible to get more dense precipitates which are easier to filter. Concentrations of ammonium salts in excess of 2 g per 100 ml, however, should be avoided, otherwise the thorium will not be precipitated completely.

Sulfate ions should be completely absent; even small amounts of sulfate lower the completeness of thorium precipitation considerably. Thus, instead of 0.0964 g of ThO_2, the amount found during precipitation with tannin in the presence of about 0.07 g SO_4^{2-} was found to be only 0.0565 g ThO_2.

Such considerable incomplete precipitation is most probably explained by the formation of the readily soluble complex salt $Th(SO_4)_2(NH_4)_4$ [8].

The tannin method of determining thorium (Table 3) posesses a rather rare sensitivity for analytical determinations of $0.0004:1000 = 4 \cdot 10^{-7}$.

Separation of Thorium from the Rare-Earths

Preliminary experiments showed that under those conditions where thorium is precipitated quantitatively, the rare-earths are not precipitated by tannin. The rare-earths are not precipitated in 0.005 N hydrochloric acid or nitric acid by tannin, only when dilute solutions are used, and their content in 100 ml does not exceed about 0.5 g. On increasing their concentration to 2 g per 100 ml, the rare-earths are precipitated in considerable amounts. In one such experiment the weight of their oxide precipitates amounted to 1.3% or 0.0265 g.

TABLE 3

Determination of Thorium in 0.005 N Hydrochloric Acid Solutions

ThO_2 taken, g	Volume of solution, ml	ThO_2 found, g	Error, g	ThO_2 taken, g	Volume of solution, ml	ThO_2 found, g	Error, g
0.0097	100	0.0096	−0.0001	0.0019	1000	0.0019	0.0000
0.0097	100	0.0098	+0.0001	0.0004	1000	0.0003	−0.0001
0.0019	1000	0.0016	−0.0003	0.0004	1000	0.0003	−0.0001

Experiments on the separation of thorium from the rare-earths were carried out mainly by the technique described below, both in nitric and in hydrochloric acid solutions. In the latter instance, when it was necessary to reprecipitate, the tannin-thorium precipitate was dissolved in hot hydrochloric acid (1:3) and reprecipitation carried out under the same conditions as those used for the first precipitation. One drawback of this method is that there occurs partial decolorization of the indicator (methyl red) during neutralization, which complicates establishment of the requisite acidity of the solution. Reprecipitation of the thorium precipitate by the same method, but using nitric acid solutions, proved impossible because of the oxidation of the tannin. The solution acquired such an intense brown color that it was impossible to establish the color change of the indicator. The precipitate obtained was, accordingly, calcined to thorium dioxide, and the latter, after weighing, was brought into solution by fusing it with potassium pyrosulfate.

TABLE 4

Separation of Thorium and the Rare-Earths by Means of Tannin

Taken, g		Volume of solution, ml	Found, g			Error	
			ThO_2				
ThO_2	TR_2O_3		First precipitation	Second precipitation	TR_2O_3	ThO_2	TR_2O_3
0,4162	0,0049	400	0,4164	—	0,0052	+0,0002	+0,0003
0,3232	0,0050	"	0,3235	—	—	+0,0003	—
0,3242	0,0050	"	0,3248	—	—	+0,0006	—
0,2705	0,2171	"	0,3062	0,2707	0,2172	+0,0002	+0,0001
0,0995	0,0990	300	0,1001	—	—	+0,0006	—
0,0471	0,1243	200	0,0486	0,0468	0,1243	−0,0003	0,0000
0,0471	0,1243	"	0,0485	0,0470	0,1248	−0,0001	+0,0005
0,0236	0,0248	"	0,0238	0,0233	0,0245	−0,0003	+0,0003
0,0050	2,0	500	0,0047	—	—	−0,0003	—
0,0024	2,0	600	0,0266	0,0025	—	+0,0001	—
0,0024	2,2	"	0,0920	0,0026	—	+0,0002	—

The results given in Table 4 show that separation of thorium and the rare-earths * proceeds satisfactorily in intric acid solutions, even when the thorium is only precipitated once, as long as the ratio of ThO_2: Tr_2O_3 is greater than unity and when separation is carried out in relatively dilute solutions. In practice, however, it is necessary to resort to reprecipitation. In all cases where satisfactory separation was achieved, the thorium dioxide was white in color, sometimes with a weak rose tint.

Method Used for Separating Thorium from the Rare-Earths.

Precipitation of Thorium. To a cold solution of the nitrates of thorium and the rare-earths free from quadrivalent cerium, sulfate ions, and hydrogen peroxide, and equal in volume to approximately half the final volume**,and containing a small amount of free nitric acid and a few drops of methyl red, ammonia is added dropwise and with stirring, until the color of the solution changes into a pure yellow. Nitric acid (sp. gr. 1.38-1.40 dilute with water in the proportion of 1:4) is then added slowly,dropwise,and with careful agitation of the solution, until the color changes to red; 3 drops per 100 ml of the final volume is then added in excess (assuming that the volume of one drop is 0.05 ml).When the concentration of the elements which we are interested in is low,then on neutralization, the precipitate of hydroxides only appears when the indicator shows an alkaline reaction; on subsequent acidification of the solution, the precipitate disappears. When appreciable amounts of these salts are present, a precipitate may appear before the solution shows an alkaline reaction, and will persist until the solution is acidified to 0.005 N; this will not interfere with the subsequent analytical procedure.

To the acidified solution is added: 0.5 g of ammonium nitrate and 1 g of tannin each(per 100 ml of the final volume) in the form of a filtered, aqueous solution; water is finally added to bring the volume up to the necessary value. When there is an appreciable amount of thorium, after addition of tannin, the white flocculent precipitate appears immediately in the cold; when the amount of thorium is low the precipitate only appears on heating. The solution contained in a beaker covered with a watch glass is heated to the boiling point. After boiling for a short time (1 minute) the hot solution is filtered through a filter paper of average density (white band). Before filtering, it is useful to add some macerated paper. When the first portion of filtrate is turbid it is recombined with the unfiltered material and passed through the filter again. The precipitate is washed with hot 0.25% tannin solution containing a small amount of ammonium nitrate (2-5 g in 1 liter). The well washed precipitate is calcined in a platinum crucible and weighed as ThO_2.

Precipitation of the Rare-Earths. Although tannin in an ammoniacal medium precipitates the rare-earths quantitatively, this method must be used with caution since the precipitate formed occupies a very large volume. When the amount of the rare-earths is small, a small excess of ammonia is added to the boiling filtrate and wash liquours from the tannin-thorium precipitate. After boiling for a short time the precipitate is transferred to a filter (red band) and washed with the same tannin solution as that used for washing the thorium precipitate. The washed precipitate is finally calcined and weighed.

It is better to precipitate larger amounts of the rare-earths with oxalic acid. But, since oxalic acid does not precipitate them completely quantitatively, the "traces" — sometimes amounting to some milligrams — remaining in the filtrate are precipitated completely with ammonia as described above. In this case, however, in addition to the "traces" of the rare-earths, other cations are also sometimes precipitated; these other ions (Ca, Fe, etc) get into the solution from insufficiently pure reagents, apparatus, etc. In order to free the precipitate from impurities, the "calcined "traces" of the rare-earths are dissolved in nitric acid and reprecipitation carried out with oxalic acid in the smallest possible amount of solution (20-30 ml).

Reprecipitation of Thorium. When the mixtures of thorium oxide and the rare-earths, prior to their separation, are colored more or less intensely brick-brown by elements of the cerium group, it is possible to get an estimate of the purity of the calcined thorium oxide from its color, since pure thorium dioxide is absolutely white in color. When the cerium subgroup is absent in the original mixture, it is not possible to estimate the degree of

*On changing the weight ratio of ThO_2: TR_2O_3 from 1:900 to 80; 1.

**Separation of the elements is most efficient when their concentration in solution is low, but it is not always possible to use strongly diluted solutions. In practice, for the separation of thorium and the rare-earths it is possible to use the following final volumes as a function of the weight of their oxides:

Weight of the oxides (g) up to	0.03	0.10	0.20	0.30	0.50 and higher
Volume of solution, ml	100	200	300	400	600

separation of thorium on the basis of the color of its dioxide, since the oxides of the yttrium group are also white or almost white, with yellow (Eu), rose (Er), and green (Tb) tints. When it is not possible to use x-ray spectrographic methods, some idea of the purity of the ThO_2 may be gained by an indirect method – by repeated precipitation of the thorium with tannin and comparing the weight of the dioxide with its weight after the first precipitation. Agreement between the results within the limits of experimental error indicates that the thorium dioxide is sufficiently pure.

For purifying it from rare-earths present as impurities, the thorium dioxide is fused with potassium pyrosulfate. After dissolving the melt in hot water acidified with nitric acid, thorium hydroxide is precipitated with ammonia. In order to achieve as complete a removal of sulfate ions as possible, the thorium hydroxide is dissolved in nitric acid and is again precipitated with ammonia. Such reprecipitation is repeated until the thorium is finally precipitated with tannin as described above. Usually, after precipitation with tannin, pure thorium dioxide is obtained. In the combined filtrates from all the thorium precipitates obtained during its purification, the rare-earths are precipitated in the form of the tannin complex and then reprecipitated with oxalic acid in the smallest possible volume.

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THE PHOTOMETRIC DETERMINATION OF ZIRCONIUM IN PHOSPHORITES BY MEANS OF PYROCATECHOL VIOLET

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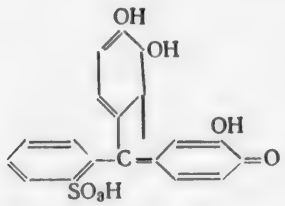
Pyrocatechol violet (3,3',4'-trihydroxyfuchsone-2"-sulfonic acid) was suggested as an indicator for the complexometric titration of various elements in 1954 [1], and has found wide application for this purpose [2].



Flaschka and Sadek [3] were the first to use pyrocatechol violet for the qualitative detection of zirconium; subsequently, Flaschka and Farah [4] developed a method for the quantitative determination of small amounts of zirconium in solutions of its pure salts and in synthetic mixtures.

We have made a study of the interaction of zirconium with pyrocatechol violet and have chosen the optimum conditions for the photometric determination of zirconium both in solutions of its pure salts and in natural materials. *

Pyrocatechol violet was synthesized according to [5] but with some small changes.

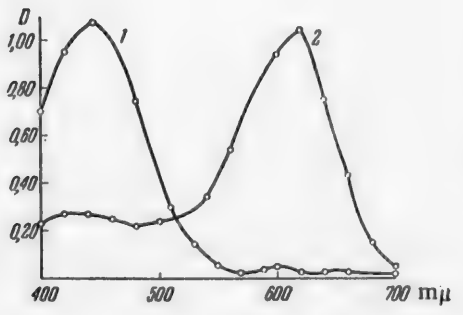


Fig. 1. Light absorption curves for solutions of the complex of zirconium with pyrocatechol violet, and for a solution of the reagent; pH 5.4.
1) $1 \cdot 10^{-5}$ M pyrocatechol violet; 2) a solution of the complex 30 minutes after mixing $1 \cdot 10^{-4}$ M $ZrOCl_2$ with $1 \cdot 10^{-4}$ M pyrocatechol violet solution.

A comparison of the light absorption curves of solutions of the reagent, and of solutions of the complex formed between the reagent and zirconium (Fig. 1.) shows that it is possible to determine zirconium in the presence of excess reagent, since in the region where the maximum absorption of the zirconium complex occurs-at a wave length of 620 mμ - the reagent itself exhibits insignificant light absorption (the maximum absorption for the reagent occurs at 445 mμ).

Since pyrocatechol violet is also an acid-base indicator, a necessary condition for the determination of zirconium (as pointed out by the authors in [4]) is the maintenance of a constant pH by the use of an acetate buffer with a pH of 5.2-5.4. In this pH range the solution of the reagent has a yellow color, while the color for solutions of the complex with zirconium is blue.

*Hafnium gives a similar reaction with pyrocatechol violet.

It should be pointed out that formation of the complex compound proceeds more rapidly after treating solutions of zirconyl chloride with concentrated acids (nitric, hydrochloric, and perchloric acids), as indicated below in the description of the determination of zirconium. This phenomenon was not discussed by Flaschka and Farah, but, as is evident from Table 1, such a preliminary treatment is of very considerable importance. The light absorption of solutions of the zirconium complex which have not been given a preliminary treatment with acids is considerably less than solutions treated with acids. Formation of the complex of zirconium with pyrocatechol violet is connected with the state of the zirconium ion in solution. There is published data on this question [6-9].

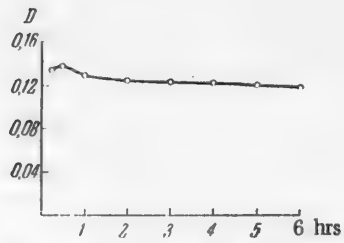


Fig. 2. Stability of the zirconium-pyrocatechol violet complex with time.

It should be pointed out that formation of the complex compound proceeds more rapidly after treating solutions of zirconyl chloride with concentrated acids (nitric, hydrochloric, and perchloric acids), as indicated below in the description of the determination of zirconium. This phenomenon was not discussed by Flaschka and Farah, but, as is evident from Table 1, such a preliminary treatment is of very considerable importance. The light absorption of solutions of the zirconium complex which have not been given a preliminary treatment with acids is considerably less than solutions treated with acids. Formation of the complex of zirconium with pyrocatechol violet is connected with the state of the zirconium ion in solution. There is published data on this question [6-9].

Maximum light absorption of solutions of the zirconium complex is observed 30 minutes after mixing the solutions of zirconium and pyrocatechol violet. After 1-2 hours the light absorption starts to drop, and after 18 hours amounts to 15-25% (Fig. 2).

Pyrocatechol violet is a highly sensitive reagent for the determination of zirconium. The color given by 0.1 γ of Zr in 1 ml of solution is quite distinct. The most suitable range for the photometric determination of zirconium covers from 5 to 70 γ of Zr in 50 ml; over this range the solutions conform to Beer's law (Fig. 3).

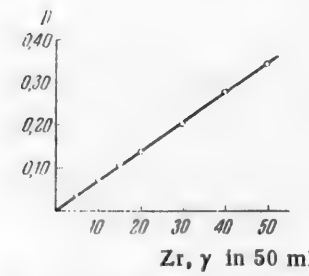


Fig. 3. Calibration curve for the determination of zirconium with pyrocatechol violet (FEK-M photocolorimeter, green filter, 20 mm cell).

When zirconium is determined in the presence of Complexon III at pH of 5.2-5.4, the alkali and alkaline-earth elements do not interfere, whatever their amounts. Other elements —Al, Fe^{3+}, Be, Ti, Th, UO_2^{2+}, Bi, V, Mo, W, Co— can be tolerated at ratios to zirconium of 100:1. Ions which possess an intrinsic intense color, such as Cu and Ni, may interfere, if they are present in amounts exceeding a ratio of metal to zirconium greater than 10:1. From what has been said above it can be concluded that the given method can be used for the analysis of alloys which contain zirconium and one or more of the elements listed above. Cl^-, NO_3^-, ClO_4^-, and SO_4^{2-} (in moderate amounts) can be present. F^-, PO_4^{3-} and also other complexing anions such as tartrate, oxalate, citrate, etc. interfere. A distinguishing feature of Flaschka and Farah's method [4] is that the reference solution used is a part of the test solution in which the color of the complex has been destroyed by addition of fluoride ions. Since fluoride ions in acid solutions corrode the cells, and, moreover, lead to complications when the test solution contains elements which also give stable complexes or insoluble compound with them (Fe, Al, Be, and Ca) we did not use their method.

In our variant the reference solution is a solution of pyrocatechol violet in an acetate buffer.

Determination of zirconium in solutions of its pure salts consists of the following.

An aliquot of a hydrochloric or nitric acid solution containing not more than 70 γ of Zr is placed in a 50 ml beaker; 5 ml of concentrated hydrochloric acid is added and the solution evaporated to a volume of about 0.5 ml. The solution is transferred to a 50 standard flask and the beaker rinsed out with three lots of 4-5 ml of water. 1 ml of 0.05 M Complexon III solution is added and the contents of the flask thoroughly mixed. The solution is neutralized with ammonia using methyl red as indicator (1 drop of 0.001% aqueous alkali solution), dilute

hydrochloric acid is then added until the solution is weak-rose in color. 15-20 ml of acetate buffer is added (pH 5.2-5.4) followed by 4 ml of a 0.001 M (about 0.04%) solution of pyrocatechol violet; the solution is made up to the mark with buffer solution and the whole carefully mixed.

The optical density is measured 30 minutes afterwards, using a FEK-M photocolorimeter with a 20 mm cell, and a green filter. The reference solution is a mixture of 4 ml of 0.001 M (0.04%) pyrocatechol violet in the acetate buffer (pH 5.2-5.4), in a volume of 50 ml. The zirconium content is determined from a calibration curve which is constructed in the same way. For the preparation of a standard solution of zirconium see [10].

TABLE 1

Effect of Preliminary Treatment of $ZrOCl_2$ Solutions with Acids, on the Light Absorption of Solutions of the Complex of Zirconium and Pyrocatechol Violet

Zr taken, γ in 50 ml	Optical density of the solution	
	Without treatment of $ZrOCl_2$ with acids, HCl, HNO_3, $HClO_4$ *	After treatment of $ZrOCl_2$ with acids, HCl, HNO_3, $HClO_4$ *
5	0,032	0,039
10	0,054	0,071
15	0,070	0,097
20	0,082	0,134
30	0,094	0,198
40	0,140	0,262

*The mean values given for the optical density were obtained on treating the solutions of zirconyl chloride with each acid taken separately.

TABLE 2

Determination of Zirconium in Phosphorites

ZrO_2 found by the photometric method, %	Mean value	ZrO_2 found by the gravimetric phosphate method* %	ZrO_2 determined spectrographically, %**
0,73; 0,74; 0,76; 0,74	0,74	0,73	—
0,84; 0,82	0,83	0,81	0,89
1,13; 1,14: 1,15	1,14	1,09	1,26
0,12; 0,12	0,12	—	0,14
0,09; 0,09; 0,08	0,09	—	0,09
0,40; 0,40; 0,40; 0,41	0,40	—	0,36
0,69; 0,71	0,70	0,68	—
1,13; 1,13; 1,15	1,14	1,26	—

*The theoretical factor of 0.463 was used for converting the phosphate to ZrO_2.

**The analyses were carried out by M. A. Petrova

For determination of zirconium in sulfuric acid solutions, an aliquot of the solution is evaporated on a sand bath to dryness until white fumes of sulfuric acid cease to be evolved; the dry residue is treated with 5 ml; it is transferred to a standard 50 ml flask and the procedure described above then followed.

Zirconium is determined in phosphorites as follows: 0.2-0.5 g of test material, depending on the expected zirconium content, is heated with 40 ml of nitric acid (1:3) for 15-20 minutes on a sand bath the solution being

contained in a 200-250 ml beaker covered with a watch glass. Since zirconium is found in phosphorites as the mineral zircon ($ZrSiO_4$), after treatment with acid, the zirconium remains in the form of an insoluble residue. The residue is quantitatively transferred onto a filter paper (blue band) and carefully washed with hot water. Filter plus residue are placed in a platinum basin, in which they are dried, ashed, and finally calcined in a muffle for 20-30 minutes. The basin is cooled and 1-3 g of potassium bifluoride is added, the mixture is fused in a muffle until a transparent melt is obtained.

To the cooled melt is added 15-20 ml of concentrated sulfuric acid and the whole evaporated on a sand bath until copious fumes of sulfuric acid are evolved. On cooling, the sulfuric acid solution is transferred from the basin into a 250 ml standard flask. in which it is made up to the mark with water and thoroughly mixed.

For determination of the zirconium, an aliquot of this solution, containing from 5 to 70 γ of Zr, is transferred to a beaker and free sulfuric acid removed by evaporation to dryness; 5 ml of concentrated hydrochloric acid is added to the dry residue and the procedure outlined above for solutions of pure zirconium salts then followed.

SUMMARY

A photometric method is described for determining from 5 to 70 γ of zirconium in 50 ml of solution by means of pyrocatechol violet. The solutions of the complex of zirconium with pyrocatechol violet conform to Beer's law. Methods have been developed for determination of zirconium in solutions of its pure salts and in phosphorites.

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DETERMINATION OF THE RATIO OF THORIUM TO URANIUM IN MINERALS AND ORES BY MEANS OF THICK-LAYER PHOTOGRAPHIC PLATES

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The thick-layer photographic plate method has been successfully used for studying the distribution of radioactive elements in rocks [1-8]. This method can be used for evaluating the amount of radioelements in materials [7,9]. For this purpose, the samples are used in their natural form (transparent sections, etc) without converting them into a powder or solution, as is usually done in the course of radiometric or radiochemical methods. Determination of the relative contents of uranium and thorium is possible on the basis of measurements of the path lengths of the α-particles in the emulsion. High energy particles are emitted by RaC', AcA, and ThC'. The α-particles emitted by RaC' from the uranium family, and by ThC' from the thorium family, are characterized by their initial energy, and, accordingly, by their path lengths in air, which at 15° and normal pressure are equal to 6.91 and 8.57 cm, respectively.

According to our measurements, the mean path length of α-particles in a photoemulsion of the type A-2 No. 2289 NIKFI is equal to 38.5 μ in the case of RaC' and 47.3 μ for ThC'. This difference of 9 μ in the path lengths of the α-particles makes it possible to calculate the number of α-particles from ThC' and RaC' fairly accurately, and, accordingly, it becomes possible to determine the relative contents of thorium and uranium in a sample.

Curie [9] in 1946 theoretically demonstrated the possibility of determining the relative contents of radioactive elements in thick layers of a mineral. According to Curie, the number of α-particles emitted from 1 cm^2 of the surface of a sample per second, with a path length greater than ρ, is equal to

$$n = \frac{N}{4} k (R - \rho), \tag{1}$$

where N is the number of α-particles emitted by 1 cm^3 of a material per second; R is the path length in air; ρ is the minimum residual path length which can be fixed, and $k = R'/R$ (R' is the path length of the α-particles in the test material).

When a radioactive material contains thorium, uranium, and actinouranium at the same time, the longest traces will belong to the α-particles emitted by ThC (8.57 cm), RaC' (6.91 cm), and AcA (6.46 cm). Accordingly, the number of α-particles which have a path length greater than 7 cm in air, and, undoubtedly belong to ThC', will be given by

$$n_1 = 0{,}663 \frac{N_{Th}}{4} k (8{,}57 - 7); \tag{2}$$

where n_1 is the number of α-particles with a path length in air greater than 7 cm.

The total number of α-particles (n), having a path length in air greater than 5.8 cm is given by

$$n = 0{,}663 \frac{N_{Th}}{4} k (8{,}57 - 5{,}8) + \frac{N_V}{4} k (6{,}91 - 5{,}8) + \frac{N_V}{4} k\, 0{,}04 (6{,}46 - 5{,}8). \tag{3}$$

Particles which have a path length in air between 5.7 and 7 cm, belong to RaC', AcA, and partly to ThC' particles which have been slowed down in the layer of the test material.

The number of α-particles with a path length between 5.8 and 7 cm (n_2) is determined by the following relationships:

$$n_2 = n - n_1 = 0{,}663\frac{N_{Th}}{4}k(8{,}57-5{,}8) + \frac{N_V}{4}k(6{,}91-5{,}8) + \frac{N_V}{4}k\cdot 0{,}04(6{,}46-5{,}8) - 0{,}663\times$$
$$\times\frac{N_{Th}}{4}k(8{,}57-7); \quad \text{or} \quad n_2 = 0{,}663\frac{N_{Th}}{4}k\cdot 2{,}77 + \frac{N_V}{4}k\cdot 1{,}11 + 0{,}04\frac{N_V}{4}k\cdot 0{,}66 - 0{,}663\frac{N_{Th}}{4}k\cdot 1{,}57 \tag{4}$$

By dividing equation (4) by equation (2) it is possible to find the relationship

$$\frac{n_2}{n_1} = 0{,}8 + 1{,}1\frac{N_V}{N_{Th}}. \tag{5}$$

By substituting the value $N_V = 1.2 \cdot 10^4$, $C_V \cdot d$ and $N_{TH} = 0.4 \cdot 10^4 C_{TH} \cdot d$ where C_V, C_{TH} are the concentrations of uranium and thorium, and d is the density of the material, we find the ratio of the concentration of thorium to that of uranium

$$\frac{C_{Th}}{C_V} = \frac{3{,}3}{n_2/n_1 - 0{,}8}. \tag{6}$$

Formula (6) makes it possible to calculate the relative content of uranium and thorium.

In the present article, which is based on Curie's calculations [9], the ratio of thorium to uranium in minerals and rocks was determined by a photographic method. It has been demonstrated experimentally that it is possible to use photoemulsions for carrying out quantitative measurements. The accuracy of measurements by the photographic method is also evaluated.

MEASUREMENT TECHNIQUE

The accuracy of calculations based on formula (6) depends on the numbers n_1 and n_2. The measurements are most accurate when the number of α-particles recorded is fairly large. For this it is possible to confine oneself to measuring the path lengths for particles which exhibit a small slope to the emulsion surface. This limitation does not affect the ratio n_2/n_1, and, consequently does not affect C_{TH}/C_U. This assumption will only be justified when the value of the slope taken is accurately established.

Measurements of path lengths with large slopes to the emulsion surface (greater than 3°), present considerable difficulties on account of the errors in measuring the depth of the track and the shrinkage factor.

For a limited number of particles measurements were made of track lengths with slopes of up to 25° to the emulsion surface.

The accuracy of measurements of the ratio of thorium to uranium drops somewhat in cases where there is an uneven distribution of the radioelements in the test samples of rock, since, in such cases, during preparation of sections only part of the grain may be captured. Errors which arise during measurement of the track lengths of long-path α-particles in the emulsion also affect the accuracy of the measurements.

The track lengths of RaC' α-particles were determined by two independent methods. The first method was based on determination of the length by the contact method. For this purpose, a transparent section 30-40 μ thick, as well as a thin layer of powder 0.5-1 μ thick (0.5 mg/cm²), were prepared from the same sample, the powder being deposited on a backing by means of a precipitation method. In order to prepare the thin layer of powder, a small amount of the uraninite was ground up with a volatile organic liquid (chloroform, alcohol, etc) and then deposited on the plate weighed beforehand. After drying, the exact weight of the powder per unit area of the surface was determined. By preparing a fine layer of powder, it is possible to achieve minimum absorption of α-particle in the radioactive material itself. The samples prepared in this way were combined with a photographic plate, which was then chemically treated and examined under the microscope. The maximum track length found for RaC' α-particles in a Type A-2 No. 2492 emulsion was 40.3 μ.

The second method of determining the path length of RaC' particles was the following. Uraninite powder together with the photographic plate were placed in a hermetically sealed cell, so that only atoms of radon and of its breakdown products could fall on the plate. After the appropriate exposure and chemical treatment, two-ray "stars" appear on the photographic plate. The path length of RaC' α-particles proved to be 40.3 μ in this case also.

Thus, for determination of the number of tracks n_1 and n_2, we assumed that particles with a path length of more than 40.3μ in the emulsion belong only to ThC', while particles having path lengths between 40.3 μ and 33.6 μ belong to RaC' and AcA.

The thick-layer photoplate method based on calculating long-path α-particles makes it possible to establish the thorium-uranium ratio for inclusions with a cross section of up to 0.1 mm^2. The study of the radioactivity of such small inclusions is very difficult by the usual radiochemical methods.

Thus the photographic method allows one to establish not only the spatial distribution of activity in a given mineral, but also makes it possible to investigate the relative content of uranium and thorium in separate parts of the test object.

EXPERIMENTAL RESULTS

Twenty radioactive minerals and ores were taken for the determination of the relative content of uranium and thorium. Transparent sections 30-40 μ thick without a cover glass were prepared from these samples, and these sections were combined with the photographic plate. After the necessary exposure, the plates were developed and examined under the microscope at a magnification of × 900. Exposure time was chosen in accordance with the activity of the sample, so that the total number of α-particles in one field of view of the microscope did not exceed 30-40, since examination of the plates is difficult when a greater number of particles is involved.

In Table 1 is given the results of measurements of the thorium-uranium ratio, and also a comparison of the results of the photographic method with those obtained by chemical and radiochemical analysis Results obtained by the photographic method are in good agreement with those of chemical and radiochemical analysis.

TABLE 1

Thorium-Uranium Ratios in Minerals and Ores

Designation of the minerals and ores, and their indices	Exposure time of the photographic plates	Area observed, cm	Measurements obtained by the photo. method: Total No. of α-particles measured	n_1	n_2	n_2/n_1	Thorium: uranium ratio by the photographic method	Thorium: uranium ratio by the chemical and radiochemichal analysis	Deviation of photographic from chemical and radiochemical results
Pitchblende No.5	35 min	0,8	212	—	212	∞	0	0	0
Uraninite 1S	35 .	0,6	131	—	131	∞	0	0	0
Black uranium silicate 1/19	46 .	1,5	264	1	263	263	0,012	0	+0,012
Radioactive mineral 7s	1 h. 49 .	1,3	242	1	241	241	0,013	0	+0,013
Pitchblende 1/8	48 .	1,5	318	1	317	317	0,01	0	+0,01
Uraninite partially replaced by pitchblende 23/10	55 .	1,3	289	2	287	143,5	0,023	0,025	—0,002
Uraninite and the pitchblende which replaces it 25/4	30 .	3,2	605	11	594	54	0,06	0,004	+0,056
Branerite V-8	1 h. 08 .	2,1	455	12	443	37,0	0,09	0,08	+0,01
Elsvortite V-3	5 . 10 .	3,2	567	40	527	13,1	0,26	0,23	+0,03
Euxenite E-20	5 . 40 .	1,2	279	37	242	6,54	0,58	0,61	—0,03
Blomstrandite V-6	6 .	2,5	417	102	315	3,08	1,44	1,44	0
Radioactive mineral 33/a	2 . 05 .	1,6	400	105	295	2,8	1,65	1.63	+0,02
Manganese ferritorite V-10	5 . 40 .	2,0	432	174	258	1,48	4,85	5,64	—0,79
Radioactive mineral No.700	2 . 55 .	1,5	331	128	203	1,58	4,23	4,42	—0,19
Ferritorite	2 . 50 .	2,4	506	212	294	1,38	5,69	5,47	+0,22
Actyusite A	5 . 40 .	2,5	476	192	284	1,47	4,9	>1	—
Ferritorite V-2	2 . 50 .	2,0	411	193	218	1,12	10,3	9,17	+1,13
Auerlite V-7	1 . 30 .	2,3	496	238	258	1,08	11,77	14,42	— 2,65
Auerlite No. 100	2 . 40 .	1,5	378	178	200	1,12	10,3	11,96	—1,66
Radioactive mineral F-11	2 . 10 .	3,2	786	366	420	1,14	9,70	—	—

The study of the radioactive minerals and ores can be divided into three groups, depending on the thorium-uranium ratio. To the first group belong samples with the indices No. 5, 1S, 4/19, 7S, 1/8, and 23/10 (Table 1), which either do not contain any thorium at all or only contain it in negligible amounts. To the second group belong the minerals and ores with the indices V-8, 25/4, V-3, E-20, V-6, and 33/A, which contain appreciable amounts of thorium as well as uranium. For these samples the thorium-uranium ratio, according to the chemical analysis, varies within the limits 0.04 to 1.63. The third group consists of the radioactive minerals and ores with the indices V-10, No. 700, 28/2, A, V-2, V-7, No. 100, and F-11, for which the ratio of thorium to uranium is greater than 4.

When thorium is absent in the test material, the thorium-uranium ratio should be equal to zero. This position is confirmed in the case of samples of pitchblende with index 5 and uraninite with the index 1S, which, according to the results of chemical analysis did not contain thorium. Thorium could not be detected in these samples by the photographic method either. We were unable to detect a single trace of a ThC' α-particle in a transparent section from the pitchblende and uraninite, the area being equal to 0.7 cm^2. The remaining minerals and ores of the first group investigated, apparently contain thorium, but in very small amounts. For example, for the samples of black silicate radioactive mineral with index 7S, and pitchblende with index 1/8 only one α-particle was found in each case, while in the case of the uraninite partially substituted by pitchblende, two ThC α-particles were found and 200 and 300 RaC' and AcA α-particles, respectively. The thorium-uranium ratio for these minerals, according to our results is very low. The deviation of the results given by the photographic method from those obtained by chemical analysis lies within the limits of experimental error.

From the results given it is clear that photographic plates can be successfully used for determining the thorium-uranium ratio in minerals and ores. The accuracy of the measurements increases in the case of minerals which keep well, when the radioelements in them are distributed uniformly. When the radioelements are distributed unevenly, it is necessary to accumulate a large amount of statistical data in order to assess the mean value of the thorium to uranium ratio.

The Error in the Determination of the Thorium-Uranium Ratio, and the Sensitivity of the Photographic Method

The error in the determination of the amount of a radioelement on the basis of a count of the number of t traces in an emulsion, is basically determined by the statistical nature of radioactive fission, and by the variation in the number of background traces of α-particles arising as a result of radioactive contamination of the photographic emulsion and the surrounding atmosphere. Accordingly, the error in the measurement of the thorium to uranium ratio will be smaller the larger the number of long-track α-particles from the test material, and the smaller the variation in background tracks.

The statistical errors in the measurement of the thorium-uranium ratio fot the materials tested with a mean value for the thorium-uranium ratio ($C_{TH}/C_U > 3$) lies within the limits 1 to 10%. For samples with a thorium-uranium ratio $C_{TH}/C_U > 3$, the error increases to 20-30%, since in this case, the ratio n_2/n_1 decreases strongly. For the samples with indices V-7, No. 100, and V-2, the statistical error exceeds the indicated value, this can be explained by the large number of ThC' α-particles.

The maximum relative deviation of the results of the photographic method from those of chemical and radiochemical analysis lies within the limits 15 to 20%.

For the quantitative determination of the radio element content of rocks it is necessary to increase the exposure time to one month and more. In addition, the exposure time cannot be made unlimited because of the presence of radioactive contamination in the emulsion itself, and in the glass, and surrounding atmosphere, and also because of the phenomenon of regression of the latent image of the particle tracks. We have shown that the effect of regression can be lowered by placing the plate which is being exposed together with the object in a cell containing nitrogen [10].

The effect of radioactive contamination in freshly prepared photographic plates is not very great. The number of background tracks found on 1 cm^2 of the surface of type A-2, No. 2492 emulsion one month after preparation of the emulsion was approximately 40, this is equivalent to 10^{-7} % U, while after three months this number increased to approximately 100 particles per cm^2. It should be pointed out that tracks of particles arising from the lower layers of the emulsion, or from the glass, are readily distinguished from the tracks of α-particles falling into the emulsion from the air. Moreover, the background tracks are distributed more or less uniformly in

the emulsion. Accordingly, their effect can be taken into account by using control plates.

In old photographic emulsions which have been kept for five-six months and longer, the effect of background tracks is considerable (about 220 per cm^2). In such cases, in order to remove the background tracks from the emulsion, the photographic plates are kept for 15 hours in a thermostat in an atmosphere saturated with water vapor at 35°, i.e. the background tracks are subjected to artificial regression. By this means α-particle tracks are almost completely removed from the surface layer of the emulsion and only some of them are preserved in its lower layers. From what has been said above it follows that by observing certain conditions (using fresh photographic plates, placing the plates in a nitrogen atmosphere, and removing the background by keeping the plates in an atmosphere saturated with water vapor, etc.) it is possible to extend the exposure time to several months, and in this way it becomes possible to carry out determinations of the activity of objects with a very low content of radioactive elements. Moreover, the photographic method can be used for studying the thorium-uranium ratio in minerals, where thorium is contained in insignificant amounts. In such cases it is difficult to measure the thorium by the emanation method because of the large influence exerted by actinon. For relatively high values of the C_{TH}/C_U ratio the presence of actinon has hardly any effect at all on the accuracy of measurements by the emanation method.

One of the drawbacks of the photographic method is the complications involved; these are the reasons which hinder its use under field conditions. All the same, when a succession of tests have to be carried out, and where detailed results are required, the photographic method, in our view, remains unreplaceable.

The limiting sensitivity of the photographic method is limited by the α-radiation of radioelements present as impurites in the emulsion, glass backing, and atmosphere. In order to take these effects into account control plates are used; by means of these plates it is possible to determine the number of background tracks on 1 cm^2, and, accordingly, corrections can be applied for them.

When freshly prepared photographic plates are used the sensitivity of the method can be increased to a content of $5 \cdot 10^{-4}$% U.

Measurements in which the background is taken into account and exposure is carried on for two months, makes it possible to carry out determination of the radioactivity down to $5 \cdot 10^{-4}$% U. In order to determine the thorium-uranium ratio the activity should be much higher, of the order of $5 \cdot 10^{-3}$% U.

TABLE 2

Thorium-Uranium Ratio in Mineral Inclusions

Mineral	No. of inclusion	Dimensions of the radioactive inclusions, mm^2	n_1	n_2	$\frac{n_2}{n_1}$	Error in determination of n_2/n_1, %	Mean value of C_{Th}/C_U	Limits of the variations in C_{Th}/C_U (from—to)
Auerlite	1	3,25	52	119	2,3	22,4	2,2	1,1—3,3
	2	1,61	26	47	1,8	34,1	3,3	2,0—8,2
	3	0,94	40	34	0,85	27,6	66,0	11,8—negative number
	4	1,41	44	38	0,86	31,2	55,0	10,3—negative number
	5	0,88	41	25	0,61	35,6	negative number	165,0—negative number
Actyusite	1	0,12	22	41	2,0	36,0	2,7	1,2—6,7
	2	0,19	0	87	—	10	0	—
	3	0,15	19	47	2,4	36	2,0	1,4—4,4
	4	0,27	39	33	0,84	35	82,5	10,0—negative number
	5	0,13	32	28	0,87	37	47,1	8,4—negative number

Variation of the Thorium-Uranium Ratio in the Minerals Auerlite and Actyusite.

During determination of the thorium-uranium ratio in the minerals auerlite and actyusite, variations in the

value of the ratio C_{TH}/C_U were detected in grains of these minerals. These minerals were found in lumps of rock in the form of fine grains with dimensions ranging from a few microns to 1-3 mm. In order to demonstrate that there is an actual variation in the thorium-uranium ratio in the grains of these minerals, we removed several grains from each mineral and determined the thorium-uranium ratio for each of them. In order to increase the accuracy repreated determinations were carried out of the thorium-uranium ratio for the same grains.

The mean value of four repeated determinations for the two minerals is given in Table 2. The table also includes the size of the grains, and the error in measuring n_2/n_1 and C_{TH}/C_U. The grain size was determined by comparison the section of the sample with the impression on a photographic plate, which was obtained by long exposures. From the mean values given in Table 2 it is clear that the ratio of thorium to uranium for the grains examined varies within the very wide limits of 2-3 to infinity.

The variations in the values of the thorium-uranium ratio for the grains of the minerals indicated lie outside the limits of experimental error. The negative value of C_{TH}/C_U, calculated by means of formula (6) signifies excess ThC' α-particles. This can be explained by the specific conditions of the emanation, or by experimental error. These values are indicated as negative values in the table. Nevertheless, the variation of the mean thorium-uranium ratio for the grains of the minerals indicated is so large, that, it presumably indicates a complex mineral composition for the "accessories", among which are included mainly uranium and thori minerals.

During a study of the mineral actyusite it was established that individual grains of this material did not contain any thorium.

Thus the thick-layer photographic plate method which is based on calculating the number of long-track α-particles, permits the establishment of the thorium-uranium ratio for inclusions with a cross section down to 0.1 mm^2 and having a weight of the order of 0.3 mg. Studies of the radioactivity of such small inclusions are difficult to undertake by the usual radiochemical methods. Thus, the photographic method permits one,not only to establish the spatial distribution of activity in a given mineral, but also gives the possibility of examining the relative thorium and uranium contents of separate parts of the test material.

In conclusion we should like to thank V. I. Baranov and A. I. Turarinov for discussions on the work and for valuable advice.

SUMMARY

It has been experimentally demonstrated that it is possible to use the photographic emulsion method for determining the relative content of thorium and uranium in minerals and ores. Measurement of the thorium-uranium ratio for $C_{TH}/C_U > 3$ can be carried out with an accuracy of 10-15% . The maximum relative experimental error for $C_{TH}/C_U > 10$ %, does not exceed 20%.

The photographic plate method is applicable to the determination of the thorium-uranium ratio in separate microinclusions or grains whose dimensions are about 0.1 mm^2, corresponding to a weight of 0.3 mg. The variations in the thorium-uranium ratio found in microinclusions is a consequence of the fact that grains of the minerals contain uranium and thorium in very different amounts.

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SPECTROGRAPHIC DETERMINATION OF TIN, ZINC, CADMIUM, ANTIMONY, LEAD, AND ARSENIC IN NATURAL WATERS

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With the introduction of hydrochemical methods into the techniques used during the search for ore deposits, analytical methods of high sensitivity are necessary which will enable the content of ore elements in natural waters to be determined at concentrations of these elements of $1 \cdot 10^{-8}$ - $1 \cdot 10^{-4}$ g/liter. In the first instance use was made of semiquantitative spectrographic analysis of the dry residues obtained from natural waters, this method permitted simultaneous determinations of 35-40 hydrogenic elements [1]. Having obtained the dry residues by evaporating 200-500 ml of water with an average mineral content (of the order of 100 mg/liter), it has been found possible to determine most of the elements with a sensitivity of $n \cdot 10^{-3}$% of the weight of the dry residue, or $n \cdot 10^{-6}$ g/liter.

This method has been widely used for studying the content of micro elements in natural waters from polymetallic deposits. Tin, cadmium, antimony, and arsenic have been detected in a comparatively small number of samples by this method [2]. These results can be explained either by the weak migration capacity of the elements indicated, or by the fact that the sensitivity of the method is not high enough. Accordingly, in order to get a final solution to the question, it was necessary to develop a more sensitive analytical method.

The most important elements to determine were tin, zinc, cadmium, antimony, lead, and arsenic, since an increased content of these elements may serve as an indication of polymetallic deposits.

A small number of papers have been published on the question of the spectrographic analysis of dry residues from natural waters [1, 3, 4]. The most well known is the use of combined spectrochemical methods based on preliminary chemical isolation of the elements to be determined, followed by spectrographic analysis of the concentrates [5-10]. Since the possibilities of a direct spectrographic analysis of dry residues are still far from being exhausted, the first part of the work described here was devoted to the quantitative spectrographic determination of tin, zinc, cadmium, antimony, lead, and arsenic directly in the dry residues from natural waters with a low mineral content.

For test materials with variable bulk composition, dry residues being a case in point, the results of spectrographic determinations depend on the composition of the samples [11]. In order to eliminate the effect of the anions on the line intensity of the test elements, the dry residues were converted into the sulfates by treatment with sulfuric acid. In order to study the effect of calcium, magnesium, and sodium, the concentration of which in natural waters varies considerably, synthetic mixtures of the sulfates of these elements were made up, the proportions of the various elements being varied within the mixtures, while the mixtures also contained small amounts of the oxides of the test elements. Evaporation curves (Fig. 1) and calibration curves (Fig. 2) were constructed; an a.c. arc operating at 16 amps was used.

It is clear from Figs. 1 and 2 that the evaporation and calibration curves for all the test elements and the base elements do not coincide with each other; thus the character of the passage of all the impurities to be determined into the arc depends on the composition of the sample.

In order to lower the effect of the bulk composition of the dry residues on the line intensities of the test

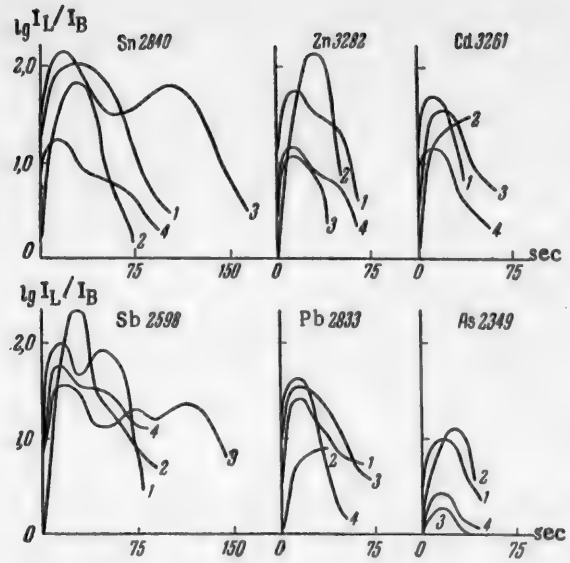

Fig. 1. Variations in the shape of the evaporation curves for Sn, Zn, Cd, Sb, Pb, and As with the main elements in the dry residues:
1) Base $CaSO_4 \cdot 2H_2O$; 2) Base-$MgSO_4 \cdot 7H_2O$; 3) base-Na_2SO_4; 4) base- a mixture of $CaSO_4 \cdot 2H_2O + MgSO_4 \cdot 7H_2O + Na_2SO_4$, consisting of equal parts by weight of the salts indicated; a.c. arc operating at 16 amp.

elements, we diluted the samples with a buffer mixture. The composition of the buffer mixture was chosen experimentally, the aim being to stabilize the evaporation conditions of the samples and the temperature of the arc flame, whatever the composition of the dry residue. The best results, which ensured the possibility of determining all six elements on one sample, were obtained on using the following buffer mixture: 50% NH_4HPO_4 16.7% $CaSO_4 \cdot 2H_2O$, 16.7% $MgSO_4 \cdot 7H_2O$, 16.6% Na_2SO_4. One part by weight of the sample was mixed with two parts by weight of the buffer mixture. In this way the contents of the main components of the mixture were levelled out in the mixtures obtained from original samples differing in composition. The addition of the disubstituted ammonium phosphate enhanced the fractional evaporation of the elements, so that the sensitivity of the determination increased.

It was established subsequently, that in order to increase the accuracy of quantitative analysis, it is advisable, in addition, to introduce an internal standard into the samples and standard mixtures. The internal standard used was germanium, the presence of which in natural waters is very unlikely (it can only be detected in very acid thermal waters having a pH of 1-2 [12]). Germanium was added to the buffer mixture in the form of germanium dioxide (0.035% GeO_2 on the weight of the mixture).

The evaporation curves show that germanium passes into the a.c. carbon arc in an identical manner to tin, zinc, and the other test elements. The calibration curves for the case where the internal standard is germanium, show that the relative intensity of the lines of the test elements in such cases, is also independent of the ratio of the calcium, magnesium, and sodium concentrations in the original samples.

In the dry residues from carbonate waters with a low mineral content, aluminum, iron, and manganese are present (on the average, 0.5% of aluminum, and 0.1% each of iron and manganese). Observations showed that the presence of these affects the relative intensity of the lines of tin, zinc, cadmium, arsenic, antimony, and lead. The experimental error thereby introduced was eliminated by using standard powders identical to the test samples with respect to their content of aluminum, iron, and manganese.

Synthetic standards were used for the analysis. The base for the standards was a mixture containing 31.00% $CaSO_4 \cdot 2H_2O$, 31.00% $MgSO_4 \cdot 7H_2O$, 30.90% Na_2SO_4, 0.15% Fe_2O_3, 0.28% $MnSO_4$, 6.67% $Al_2(SO_4)_3 \cdot 18H_2O$. The iron, manganese, and aluminum contents of this mixture, expressed as the metal, were 0.1, 0.1, and 0.5% wt. respectively. The composition used for the base of the standards is the nearest approximation to the mean content of calcium, magnesium, sodium, iron, manganese, and aluminum in the dry residues from carbonate waters with a low mineral content. By adding the oxides of the test elements to this base mixture, a primary standard containing 0.1% each of tin, zinc, cadmium, antimony, lead, and arsenic was obtained.. Standards with lower contents of the elements right down to 0.0001%, were prepared by successive mixing of one part of the primary standard with two parts by weight of the base.

Further, both the standards and samples – the dry residues from natural waters – were mixed with a buffer mixture of the composition indicated above, containing germanium as the internal standard; to two parts by weight of the buffer mixture was added one part by weight of the test sample (or standard). Mixing of all materials, both during the preparation of standard powders, and during the dilution of samples with the buffer mixture, was carried out by careful grinding in an agate mortar in the presence of alcohol.

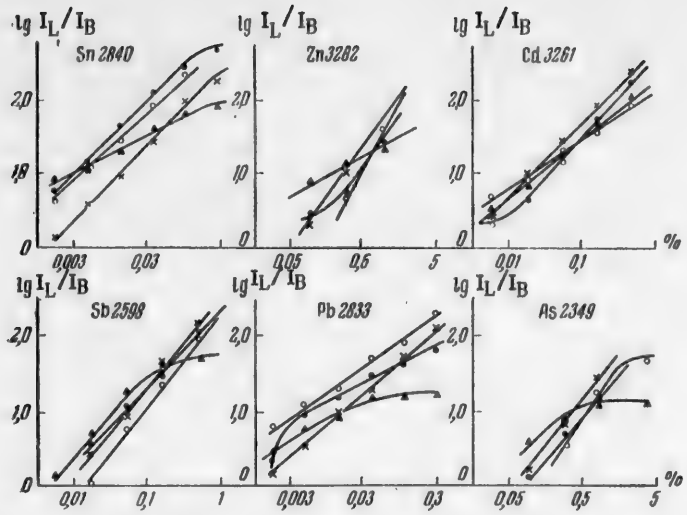

Fig. 2. Displacement of the calibration curves for Sn, Zn, Cd, Sb, Pb, and As caused by changes in the composition of the base of the dry residue.
x) Base- $CaSO_4 \cdot 2H_2O$; △) base- $MgSO_4 \cdot 7H_2O$; o) base- Na_2SO_4; O) base- a mixture of $CaSO_4 \cdot 2H_2O + MgSO_4 \cdot 7H_2O + Na_2SO_4$ consisting of equal parts by weight of the salts indicated. a.c. arc, i = 16 amp , complete burning.

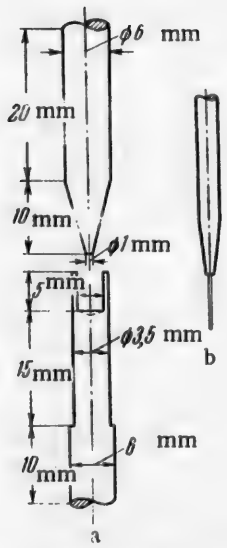

Fig. 3. Shape and dimensions of the graphite electrodes (a), and the tamper (b) with a needle for packing down the samples. Dimensions in mm.

All the materials used were checked beforehand for the absence of the elements to be determined in them.

The mixtures obtained were weighed out on a torsion balance in 15mg portions. Each portion of powder was placed in the canal of the lower graphite electrode and compressed with a special tamper (Fig. 3).

Samples and standards were fired in a vertically arranged 16 amp carbon a.c. arc at a voltage of 220 volts. The arc was supplied from a DG-1 generator with a discharge gap in the arc circuit of 0.45 mm. The distance between the electrodes was kept equal to 2 mm during arc burning. The spectra from two carbons was taken on one place on the photographic plate. Each exposure time was 30 seconds (total exposure was one minute). The duration of arc burning was established on the basis of the evaporation curves.

The spectra were photographed on an ISP-22 quartz spectrograph with a three-lens illuminating system; the slit width of the spectrograph was 0.012 mm; which the plates used were "Spectrographic type " with a sensitivity of not less than 16 GOST units. The plates were developed at 18° for 3 minutes in a high-contrast metol-hydroquinone developer.

The table contains details of the analytical lines used, and also comparative results illustrating the sensitivity of determination under the conditions of the method developed, and under the conditions used for semiquantitative analysis as described in [3].

It should be pointed out that during the determination of low concentrations of elements in dry residues (approximating to the limit of the sensitivity of detection of the elements), the intensity of the lines is comparable

in magnitude to the intensity of the background: $I_L = I_{Back.}$ [13, 14]. Accordingly, during measurement of the relative intensity, the background intensity is excluded beforehand from the intensity of the impurity lines and the reference lines. The choice of where to make the measurements of the background on the spectrograms was made on the basis of a method suggested by Filimonov [15, 16]. Experiments which we carried out showed that it is best to measure the background as minimum blackening directly in the neighborhood of the analytical lines. For the lines Sn 2840.0; Sb 2598.1; Cd 3261.0; As 2349.8; Ge 2754.6 the background was measured on the short-wave side of the analytical lines, while for the lines Zn 3282.3 and Pb 2833.1 the background was measured on the long wave side of the analytical lines.

Test element	Analytical line, A	Sensitivity of the determination, %		Test element	Analytical line A	Sensitivity of the determination, %	
		By semi-quantitative analysis	By quantitative analysis *			By semi-quantitative analysis	By quantitative analysis *
Tin	2840.0	$1 \cdot 10^{-3}$	$1.3 \cdot 10^{-4}$	Antimony	2598.1	$1 \cdot 10^{-2}$	$1.2 \cdot 10^{-3}$
Zinc	3282.3	$1 \cdot 10^{-1}$	$3.7 \cdot 10^{-3}$	Lead	2833.1	$1 \cdot 10^{-3}$	$4.3 \cdot 10^{-4}$
Cadmium	3261.1	$1 \cdot 10^{-2}$	$1.2 \cdot 10^{-3}$	Arsenic	2349.8	$1 \cdot 10^{-1}$	$3.7 \cdot 10^{-3}$

*The 2754.6 A of the internal standard, germanium, which is common to all the test elements, was used for the quantitative determinations.

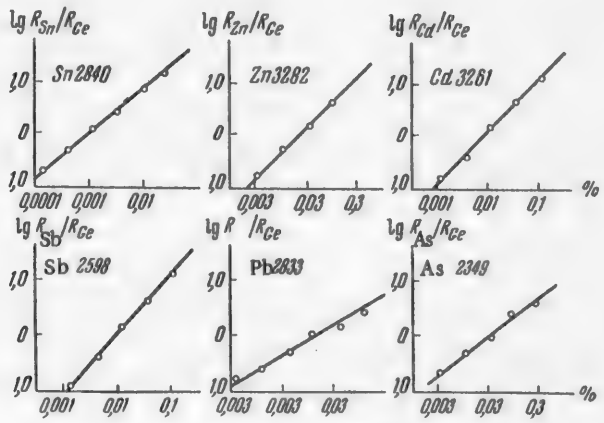

Fig. 4. Calibration curves for the determination of Sn, Zn, Cd, Sb, Pb, and As.

The blackening of the lines and of the background around them was measured on a MF-2 microphotometer. Conversion from blackening to intensity, and elimination of the background intensity $I_{Back.}$ from total intensity of line and background $I_{n + Back.}$ was carried out by means of a calculator based on the characteristic curve of the photographic plate.

The calibration curves were constructed within the coordinates log $R_{El.}/R_{Ge}$; log C, where $R_{El.} = I_{El.}/I_{Back.}$ El is the ratio of the line intensity of the test element to the background intensity near this line, and $R_{Ge} = I_{Ge}/I_{Back.}$ Ge is the ratio of the line intensity of the internal standard, germanium, to the background intensity near this line, and C is the concentration of the test element.

For a single determination, one spectrogram of the sample was used in conjunction with a calibration curve, each point of which was obtained by meaning the results of the photometric measurements of one spectrogram of each standard.

On the basis of 170 control analysis of mixtures of the sulfates of calcium, magnesium, and sodium with

known contents of the test elements, it was established that the mean probable error of a determination amounts to ± 12% relative.

The technique developed permits quantitative determination of the test elements in the following concentration ranges: tin from 0.00013 to 0.1%; zinc from 0.0037 to 0.1%; cadmium from 0.0012 to 0.1%; antimony from 0.0012 to 0.1%; lead from 0.0004 to 0.1%; and arsenic from 0.0037 to 0.1%.

It should be possible to determine copper. Where this is done however, contamination of the spectrographically pure carbon electrodes by copper should be borne in mind.

Using the method developed, tin, zinc, cadmium, antimony, lead, and arsenic were quantitatively determined in 155 dry residues from carbonate waters with a low mineral content. The enhanced sensitivity of the method made it possible to detect tin in 143 cases as against 99 found previously by semiquantitative analysis, zinc was found in 87 instead of 37, lead in 154 instead of 91, antimony in 15 instead of 1, and arsenic in 20 instead of 10. Cadmium was not detected in any of the dry residues tested.

SUMMARY

A method has been developed for the quantitative spectrographic determination of $1.3 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$% of tin, $4.3 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$% of lead, $1.2 \cdot 10^{-3}$ - $1 \cdot 10^{-1}$% antimony and cadmium, and $3.7 \cdot 10^{-3}$ - $1 \cdot 10^{-1}$% of zinc and arsenic in the dry residues obtained from natural waters with a low mineral content; the probable error of a single determination is ± 12% relative. Determination of copper is possible but contamination of the spectrographically pure carbon electrodes by the copper must be borne in mind.

By means of the method developed, tin, zinc, antimony, lead, and arsenic have been determined in 155 dry residues from carbonate waters with a low mineral content. Cadmium was not detected.

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ANALYTICAL APPLICATIONS OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 4. THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF MANGANESE *

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The published literature on photometric methods of determining manganese is comparatively poor. In the first instance mention should be made of the different variants of the general method of determining manganese, based on its oxidation to the permanganate ion [1-7]. This method is very specific and allows determination of manganese in most natural objects without its preliminary separation from other foreign elements. Appreciable concentrations of colored ions and chlorides interfere. In many instance, however, the sensitivity of the reaction is insufficient for determination of traces of manganese without its preliminary concentration.

Divalent manganese ions in alkaline solution react with formaldoxime to form a reaction product which colors the solution brown [8-9]. Iron and other elements interfere. Schroder has suggested a photometric method for the determination of trivalent manganese ions which are formed during the oxidation of Mn^{2+} in a medium of phosphoric and perchloric acids [10]. It has also been suggested that manganese be oxidized to the trivalent state by means of bromate in a medium of 8 N N_2SO_4 [11]. Using this method it is possible to determine from 2 to 70 mg of Mn in 100 ml of solution photometrically. Specker, Hartkamp, and Kuchtner [12] have suggested photometric determination of the diethyldithiocarbamate of trivalent manganese. Lukina, Osetrova, Karanovich, and Chernitskaya [13] have studied salicylal-o-aminophenol as a reagent for manganese. The mechanism of the reaction of Mn with this reagent is catalytic. The authors have shown that it is possible to determine manganese in the presence of μgram amounts of certain foreign elements. It has been suggested that manganese can be determined by means of the violet color of the complex pyrophosphatomanganic acid, but the sensitivity of this reaction is low [14]. A number of other methods based on oxidation of organic compounds by the permanganate ion have not found practical application. Reactions of this type are very sensitive but not very specific[7].

Compared with a number of other elements, divalent manganese does not display a strong chromophoric action, accordingly few sensitive reactions are known for this element which are based on the formation of intensely colored complex compounds with organic reagents. In this connection the thiooxine reaction is of considerable value for the photometric determination of manganese.

In alkaline and ammoniacal solutions (in the presence of tartrates and citrates) divalent manganese reacts with thiooxine to form a brown colored inner-complex salt. This can be prepared in a pure form by adding a solution (1:100) of manganese chloride dropwise and with stirring to excess of a freshly prepared and filtered solution of potassium thiooxinate containing sodium tartrate. The brown, amorphous precipitate of the manganese complex is slowly filtered off under suction, washed several times with water and then with alcohol and dried in a vacuum oven at room temperature.

Found % Mn 14.55; S 16.91; N 7.55 $Mn(C_9H_6NS)_2$. Calculated % Mn 14.66; S 17.06; N 7.46.

*Communication 3, see J. Anal. Chem. 13, 643 (1958).

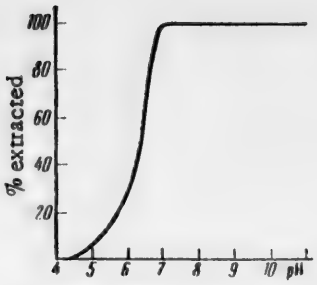


Fig. 1. Extractability of manganese thiooxinate as a function of the pH of the medium.

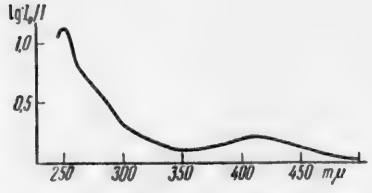
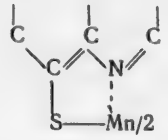


Fig. 2. Absorption spectrum of a 0.000033 M solution of manganese thiooxinate in chloroform.

Manganese thiooxinate is insoluble in water, but is readily soluble in most organic solvents to give solutions which are colored an intense brown. It is sparingly soluble in carbon disulfide and carbon tetrachloride. It is insoluble in aliphatic hydrocarbons. Extracts of manganese thiooxinate in toluene, benzene, chlorobenzene, and xylene, are stable for two days. On keeping for a longer time, the extinction of the extracts gradually decreases. Solutions of manganese thiooxinate in chloroform and bromoform are less stable (presumably, because of the enhanced photochemical sensitivity of these solvents). Chloroform solutions of manganese thiooxinate are destroyed in a matter of minutes under the action of short-wave ultraviolet radiation.

Because of the instability of MnS in acid solutions, and because of the incapacity of manganese to form stable coordination bonds with nitrogen, one could hardly expect formation of a highly stable five membered ring with the following group



Actually, as is evident from Fig. 1, manganese thiooxinate is only stable in alkaline solutions and is extracted at pH > 7.

The limits within which manganese thiooxinate can be extracted were investigated as follows. 40 γ of Mn was added to a buffer mixture with a certain pH contained in a separating funnel. The solution was made up to 50 ml with the same buffer, and 2 ml of a 3% alcoholic solution of thiooxine dihydrate $C_9H_6NSH \cdot 2H_2O$ added; the manganese thioxoinate was then extracted with 10 ml of toluene. The amount of manganese was determined by means of a calibration curve.

Manganese thiooxinate prepared as described above was used for taking the absorption spectrum. The spectrum was registered on a SF-4 spectrophotometer, the chloroform solution of the manganese complex being frequently changed because of the destructive effect of the ultraviolet radiation on manganese thiooxinate.

As is evident from Fig. 2, the light absorption curve for manganese thiooxinate has two maxima: at $\lambda_1 = 250$ mμ (molar extinction coefficient $\epsilon_1 = 34{,}000$) and at $\lambda_2 = 413$ mμ (molar extinction coefficient ϵ_2 about 7,000).

Conformity to Beer's law was studied by the same method, using the same sequence of operations as those described for studying the extractability of manganese thiooxinate as a function of the pH of the solution.

As is evident from Fig. 3, solutions of manganese thiooxinate in carbon tetrachloride conform to Beer's law down to 4 γ in 1 ml of CCl_4.

Thiooxine in aqueous solutions only reacts with those elements which form sulfides which are stable to the action of water. The alkali and alkaline-earth metals, as well as Al, Cr, Zr, Th, Ti, La etc, even in appreciable concentrations, do not interfere with manganese determination.

In view of the fact that the thioxine reaction for manganese is carried out in an alkaline medium, its specificity (without resorting to masking complexing agents) is low, since, in alkaline solutions, most elements which form sulfides which are stable to the action of water react with thiooxine. The only exceptions are those elements which exist in alkaline solutions in the form of very stable anions. In the given instance, this is mainly true of molybdates, tungstates, and arsenates. Potassium cyanide is used for masking iron, nickel cobalt, palladium, and some other elements in their lower valence states. In the form of their cyanide complexes these metals do

not interfere with the determination of manganese. The cyanide complex of manganese has a low stability at pH 10 and interacts with thiooxine to form manganese thiooxinate.

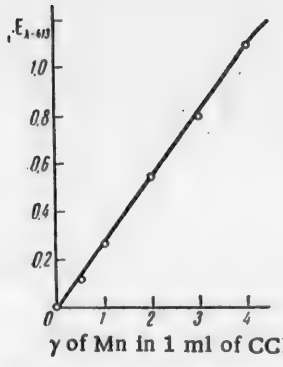


Fig. 3. Conformity to Beer's law of solutions of manganese thiooxinate in carbon tetrachloride (light filter S = 42).

It is very important to complex iron completely as the complex ion $[Fe(CN)_6]^{4-}$, this can only be achieved under very strictly defined conditions. None of the variants of this method of masking iron used by other research workers proved suitable in our case. Using these variants some of the iron always remained uncomplexed. After numerous experiments we became convinced that in order to bind iron completely as the complex $[Fe(CN)_6]^{4-}$ two conditions must be fulfilled: 1) iron must be completely reduced to the divalent state, ascorbic acid is the best reducing agent for this purpose (other organic reducing agents proved to be insufficiently active); 2) complexing of the iron as the cyanide complex should be carried out at a pH of 9.5-10.5. At lower or higher pH values, complexing of iron is incomplete. Silver and gold in alkaline solutions are reduced to the metals and do not interfere with the determination of gamma amounts of manganese. Of the platinum metals, the effect of Pt, Pd, Ir, and Os was studied. Platinum in amounts of 20 mg, under the conditions of the method developed, colored the extract an intense blue. The behavior of smaller amounts of Pt (1-2 mg) was not studied.

Palladium, iridium, and osmium in milligram amounts do not interfere with manganese determination. Lead, zinc, cadmium, thallium, vanadium, and tin should be absent.

Determination of Manganese in the Presence of Various Elements (taking 5 γ Mn)

Foreign element (Me), mg	Ratio Mn : Me	Mn found, γ	Foreign element (Me), mg	Ratio Mn : Me	Mn found, γ
Fe^{III}—5	1 : 1000	5,0	As^{V} —10	1 : 2000	4,8
Cu^{II} —3	1 : 600	4,8	Hg^{II} —0,05	1 : 10	5,1
Ni^{II} —15	1 : 3000	4,7	Ag—10	1 : 2000	4,9
Co^{II} —10	1 : 2000	5,1	Au^{III}—20	1 : 4000	5,2
Pd^{II} —20	1 : 4000	5,1	Os^{VIII} —5	1 : 1000	5,0
Mo^{VI}—30	1 : 6000	5,0	W^{VI}—20	1 : 4000	5,0
Sb^{III}—1	1 : 200	4,9	Re^{VII}—10	1 : 2000	5,1
Bi^{III}—0,02	1 : 4	5,2	Ir^{IV}—15	1 : 3000	5,2

Using a SF-4 spectrophotometer for optical measurements, and using 5 ml of extracting agent for the extraction, it is possible to determine as little as 1.5 γ Mn with satisfactory accuracy. Using 10 ml of extracting agent and a Pulfrich photometer, it is possible to determine 3 γ Mn in 50-100 ml of solution.

Preparation of Reagent Solution.

A solution of thioxine in carbon tetrachloride in which the concentration is 35 mg/liter is used. Such a solution is best prepared by extracting a suspension of thioxine dihydrate with carbon tetrachloride, the suspension having been prepared by neutralization of concentrated aqueous solutions of thioxine salts. When this technique is used, the thioxine passes into the organic solvent layer in the anhydrous state – C_9H_6NSH. From its solution in CCl_4, on shaking water, a considerable amount of the thioxine passes into the aqueous phase in the form of the dihydrate $C_9H_6NSH \cdot 2H_2O$.

Thioxine solutions in CCl_4 have a very weak yellow color and are stable for a minimum of one month. The stability of the solutions is strongly dependent on the purity of the carbon tetrachloride.

a) Preparation of a Solution from Thiooxine Hydrochloride. 4.28 g of thioxine hydrochloride is placed in a 250 ml separating funnel and 10 ml of twice-distilled water added. On shaking, the thioxine hydrochloride

first dissolves, and then a thick bright-red crystalline precipitate of thiooxine dihydrate separates out. 100 ml of CCl_4 is added to the separating funnel and the whole thoroughly shaken, most of the red crystals disappear. 3-4 ml of a 10% solution of sodium acetate is then added, and shaking continued for several minutes until the red precipitate has dissolved completely in the CCl_4. The CCl_4 layer which has a yellow color is separated from the aqueous phase and slowly filtered through a plug of cotton wool.

b) From the Potassium Salt of Thiooxine. 5.11 g of potassium thiooxinate $C_9H_6NSK \cdot 2H_2O$ is dissolved in 10 ml of twice-distilled water, and neutralized with 1.5 ml of glacial acetic acid. The thioxine dihydrate which is precipitated is extracted with 100 ml of CCl_4 as described above. 3 ml of 10% sodium acetate solution is added and the extraction continued for several minutes. The CCl_4 layer is removed and filtered as described above.

Analytical Procedure

To 15-20 ml of a weakly acid test solution contained in a 100 ml Erlenmeyer flask is added 2 ml of a 5% solution of ascorbic acid, and the pH of the solution is ad usted to a value of 7-8 by dropwise addition of 5% NaOH solution; 5 ml of 5% KCN solution is then added and the whole heated to the boiling point. The cooled solution is transferred to a separating funnel and the flask rinsed with two 3 ml portions of a buffer solution (46 g $Na_2B_4O_7 \cdot 10H_2O$ and 9 g KOH per liter) and the total volume in the separating funnel made up to 50 ml with the same buffer solution; the pH at this stage should be about 10. 1 ml of the solution of the reagent in CCl_4 is added and the whole shaken vigorously for 1 minute, when 9 ml of pure CCl_4 is added and shaking continued for a further 3 minutes. The extract is allowed to stand and is then transferred to a second separating funnel after carefully separating it from the aqueous phase. Another 3 ml of pure CCl_4 is added to the first separating funnel and the contents shaken up. After the layers have separated, the second extract is combined with the first extract in the second separating funnel, care being taken to prevent any of the aqueous phase from getting into the second funnel.

25-30 ml of water acidified with hydrochloric acid so that the pH is exactly 3, is added to the second funnel and the whole shaken vigorously for 3 minutes. During this process the manganese passes completely into the aqueous phase, while foreign elements accidentally partially extracted during the first extraction remain in the extract. After the layers have separated out, the carbon tetrachloride is rejected, while the aqueous phase is washed with two lots of 5 ml of pure CCl_4.

The aqueous phase is transferred to a 100 ml flask and 2 ml of a 5% ascorbic acid solution added, the pH is adjusted to 7-8 by means of 5% NaOH, and 5 ml of 5% KCN solution added; the mixture is finally heated to the boiling point. The cooled solution is transferred to a separating funnel and the flask rinsed with two lots of 3 ml of the buffer solution mentioned above; the total volume of solution in the separating funnel is made up to 50 ml with the same buffer solution. 1 ml of the carbon tetrachloride solution of the reagent is added and the while vigorously shaken for 1 minute, 9 ml of pure CCl_4 is added and the shaking continued for a further 3 minutes. The manganese thiooxinate extract is separated, and filtered through a cotton wool plug; the solution is measured photometrically at 413 $m\mu$, or by means of a S-42 light filter, and the amount of Mn determined by means of a calibration curve; the latter is constructed using pure solutions of manganese, all the reagents mentioned above being used.

Results obtained by this method are given in the Table.

SUMMARY

1. The interaction of thiooxine with divalent manganese has been studied. Manganese thioxinate $Mn(C_9H_6NS)_2$ is insoluble in water and is readily extracted by most organic solvents to give solutions with an intense brown color.

2. A photometric method has been developed for the determination of small amounts of manganese. In the presence of potassium cyanide, the method permits determination of Mn^{2+} in the presence of considerably greater amounts of many elements (Fe, Cu, Ni, Co, Pd, Mo, Sb, As, Ag, Os, W. Re and Ir).

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ISOTOPIC ANALYSIS OF WATER

M. Ya. Kats and F. S. Lapteva

Various methods have been described for the isotopic analysis of water [1-6],* they include optical, mass-spectrometric, and densitometric methods, and those based on the magnetic momenets of the nuclei, etc. We have developed a method for the isotopic analysis of water which is based on isotopic exchange between water and carbon dioxide, and on measurement of the density by a differential pyknometric method. By carrying out the isotopic reaction between water and CO_2 at 50-100 atmospheres and 90° the possibilities of determining the concentration of the heavy isotopes of oxygen in water are extended as compared with other methods, in which this reaction is carried out at atmospheric pressure and room temperature [2-3]. From the decrease in density of water enriched with O^{17} and O^{18}, as a result of a one-stage isotopic exchange reaction with CO_2, it is possible to determine the concentration of the heavy isotopes of oxygen in the original water. By means of several analogous reactions the isotopic composition of the oxygen of water can be readily reduced to its normal compositon.** In the variant we have developed of the differential pyknometric method of determining density*** the effect of variations in the temperature of the thermostat is considerably reduced, this means tha in the case of mass analyses measurement is essentially simplified, and te error of the pyknometric method is decreased ($\pm 10^{-6}$ g/cm^3) in comparison with published results [3].

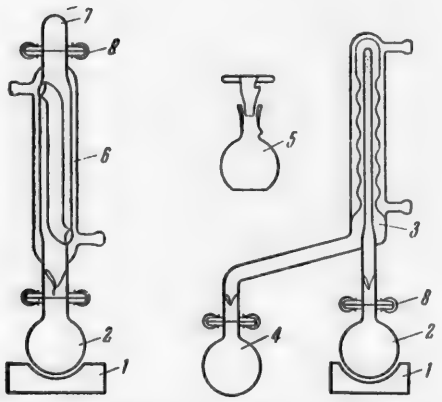

Fig. 1. Flask heater; 2) boiler; 3) vertical straight condenser; 4) condensate receiver; 5) quartz condensate receiver (for the last distillation); 6) reflux condenser; 7) cover; 8) clip.

The dimensionless magnitude $\Delta\rho/\rho_0 = (\rho - \rho_0)/\rho_0$ where ρ is the density of the test water and ρ_0 is the density of the standard water, characterizes the increase in density on increasing the concentration of deuterium and the heavy isotopes of oxygen (O^{18} and O^{17}). Similarily, we designate by $\Delta\rho_D/\rho_0 = (\rho_D - \rho_0)/\rho_0$ and $\Delta\rho_k/\rho_0 = (\rho_k - \rho_0)/\rho_0$ the increase in density of the water following upon an increase in the concentration of deuterium only, or upon an increase in the concentration of the heavy isotopes of oxygen only, respectively (ρ_D is the density of the test water; in which only the deuterium concentration is higher than in the standard water; ρ_k is the density of water in which which only the concentration of the heavy isotopes of oxygen is higher than in the standard water). It is assumed that $\Delta\rho_D/\rho_0$ and $\Delta\rho_k/\rho_0$ are independent. Then it is obvious that $\Delta\rho/\rho_0 = \Delta\rho_D/\rho_0 + \Delta\rho_k/\rho_0$.

ρ_D/ρ_0 and ρ_k/ρ_0 are determined experimentally. On the basis of these results the concentration of deuterium C_D is calculated as well as a certain effective concentration of heavy isotopes of oxygen $C_k \cong c_{18} + 0.5\, c_{17}$.

*References are only made to reviews and recent original work.

**By normal isotopic composition is meant the isotopic composition of the oxygen in standard water(in our experiments Moscow tap water).

***The first variant of the method described for measuring density was developed and used for controlling technological processes under the leadership of M. I. Kornfel'd in 1944-1945.

Purification of the Water

When the water does not contain appreciable amounts of impurities, in particular organic materials, then it is sufficient to: a) boil the water under reflux for about one hour in the presence of potassium permanganate; b) carry out a three-fold distillation, rejecting the initial and final fractions (10% of the volume of liquid distilled). In such cases, the error in determining the ratio ρ/ρ_0 arising from insufficient purification of the water is considerably less than $1 \cdot 10^{-6}$. When appreciable amounts of organic impurities are present, in addition to the two processes outlined above, the water is preliminarily purified by oxidation of impurities on a catalyst (e.g. cupric oxide) at a temperature of about 700° by a stream of oxygen. * Control measurements showed that the electrical conductivity of the purified water was less than 10^{-5} ohm^{-1} cm^{-1}

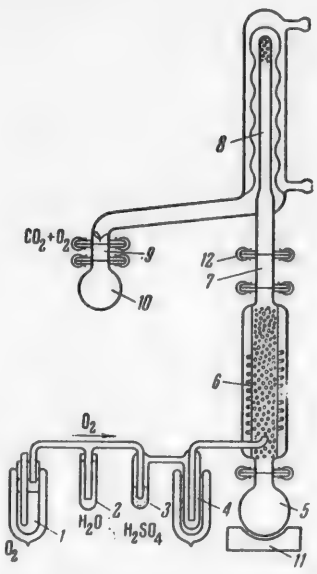

Fig.2. 1)Dewar vessel containing liquid oxygen; 2) pressure limiter; 3) sulfuric acid trap; 4) trap cooled with liquid air; 5) boiler; 6) quartz oven containing the catalyst; 7) connecting joint; 8) condenser; 9) connecting joing with opening; 10) receiver; 11) flask heater; 12) clip.

For low and average concentrations of deuterium the distillation apparatus composed of plane standard ground joints (Fig. 1), is used, this is very convenient for mass analyses. The apparatus used for oxidizing impurities at high temperatures is shown in Fig. 2. Before an analysis the apparatus is freed from traces of water remaining from a previous analysis by purging with hot air.

A quartz apparatus (Fig. 3) is used for purifying water with a high deuterium concentration. During the collection of the first fractions from each distillation, the dropper is placed in position a; when the purified product is being collected the dropper is rotated on the joint into position b. The inner tubes in the first two straight condensers are conical; in operation, the narrow opening (diameter 3 mm) of the preceding condenser is sealed with a drop of water. The assembled apparatus is heated and dried under a vacuum for about one hour. A few ml of the test water is introduced into the flask, and, by heating the apparatus, all this water is pumped off (it is collected in trap 5), i.e. the apparatus is washed with the vapors of the test water. Dried air is let into the apparatus and a few crystals of dry permanganate placed in the flask, the test water is then introduced. The apparatus is connected to the atmosphere through two traps containing liquid air. The water is first boiled under reflux, the cooling is then stopped, and the original fraction which is to be rejected is then distilled to dryness through the remaining flasks of the apparatus into the dropper offshoot, while the middle fraction is distilled into the second flask. Before starting the second distillation the flask with the reflux condenser is cooled (by immersing it in tap water). The second and third distillations are then carried out in the same way, all the three original fractions being collected in the dropper offshoot, while the final fractions remain in the flask-boilers.

The standard water is purified in the same way in the same apparatus as that used for purifying the test water. Prior to filling the pyknometers the purified product and the standard water are kept in quartz vessels.

Calibration of the Pyknometers

Quartz (preferably) or glass pyknometers with a capillary diameter of about 0.1 mm, and 15 mm long were used [3, 7]. Since the density of the water is measured independently twice, and each measurement is carried out in two pyknometers, it is necessary to choose four approximately similar pyknometers. They are annealed until their weights are similar within the sensitivity of the balance.

The pyknometers are first rinsed with water (2-3 ml), dried under vacuum, and then filled. The filler makes it possible to fasten the pyknometer with the funnel either underneath (with the capillary on top) and the

*After such an operation, only the deuterium concentration can be determined accurately.

cover on top, or vice versa (Fig. 4). Water poured into the pyknometer serves as a lubricant for the conical ground joints of the pyknometers. By successively changing the pressure in the filler, the water is poured into the pyknometers and then degassed under vacuum until no more bubbles are evolved from the pyknometers. If, during this operation, the upper part of the capillary is not filled, then by gentle heating (e.g. in the hand) the water will expand, and the last bubble of air will be expelled from the capillary. That the capillaries are completely full is readily observed in the light. For control, the filled pyknometers are held under suction for a few minutes. In order to pour the water out of the pyknometer, it is necessary to introduce some bubbles of air into it beforehand, and then successively change the pressure in the filler.

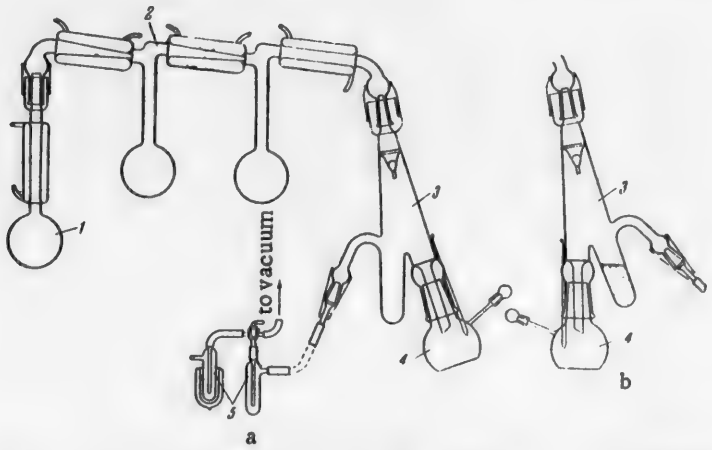

Fig. 3. 1) Distillation flask with a reflux condenser; 2) intermediate boiler with straight condenser; 3) dropper; 4) flask for the purified product; 5) trap with liquid air.

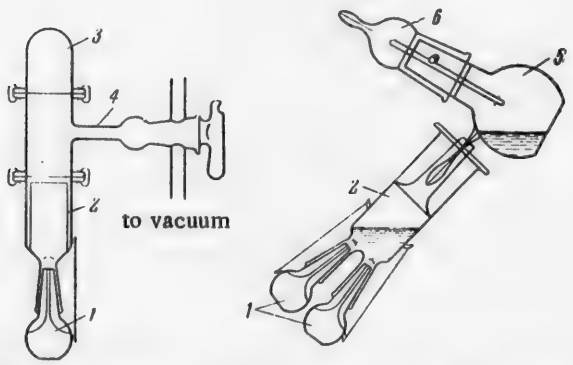

Fig. 4. 1) Pyknometers; 2) filling funnels; 3) cover; 4) filler; 5) quartz for water with high concentrations; 6) cover for it.

The pyknometers filled with standard water are placed in the cradle of a rotating stirrer (rotated by means of a Warren motor at 60 revolutions/minute) in a thermostat, the temperature of which is kept 2-4° above room temperature. The level of the water in the thermostat should be such that the joints of the pyknometers stick out above the surface of the water in the thermostat (about 10 mm). Both pyknometers appear successively in the

same places in the thermostat. The difference between the temperatures of both pyknometers wil be, at least, of one order less than the variations in temperature of the thermostat which is readily maintained with an accuracy of ± 0.01° when an ultrathermostat type TS-15 is used. Large pyknometers (25 ml) should be kept in the thermostat for 40 minutes, while small ones (10 ml) should be kept for 30 minutes. During this period the pyknometers acquire the temperature of the thermostat and a drop of water appears on the end of the capillary and dries out gradually. It is essential to ensure that the ends of the capillaries become dry simultaneously. Where necessary a filter paper can be used for removing part of a drop from the end of one of the pyknometers. Both pyknometers are removed simultaneously from the thermostat, and, after 15-20 minutes, wiped with alcohol, and placed on different pans of a balance. The balance used in the course of our work was one with a sensitivity of $\pm 10^{-5}$ g, and capable of handling a maximum load of 50 g. As a rule, one of the pyknometers filled with standard water is heavier than the other. Weights are added to the lighter pyknometer and the balance readings determined.

TABLE 1

$\Delta\rho/\rho_0$ at 25°	Correction	$\Delta\rho/\rho_0$, at 25°	Correction	$\Delta\rho/\rho_0$, at 25°	Correction	$\Delta\rho/\rho_0$, at 25°	Correction
0	0	0,01	0,000080	0,07	0,000230	0,107	0,000008
0,0001	0,000001	0,03	0,000220	0,09	0,000140	0,107720	0
0,001	0,000012	0,05	0,000260	0,1	0,000070		

In order to diminish the effect of variations in the density of air, both pyknometers should have volumes as near as possible to each other (within about 0.5 ml for pyknometers with a volume of about 10 ml and within the limits of about 1 ml for pyknometers with a volume of about 25 ml).

The true weight of the standard water in the volume of the pyknometer at the thermostat temperature is given by: $P = P_1 - P_0$, where P_0 is the true weight of the dry pyknometer, and P_1 is the true weight of the pyknometer plus standard water at the thermostat temperature. Reduction of the weighing results to weights in vacuo is carried out by taking into consideration the density of quartz, water, brass weights and the small weights.

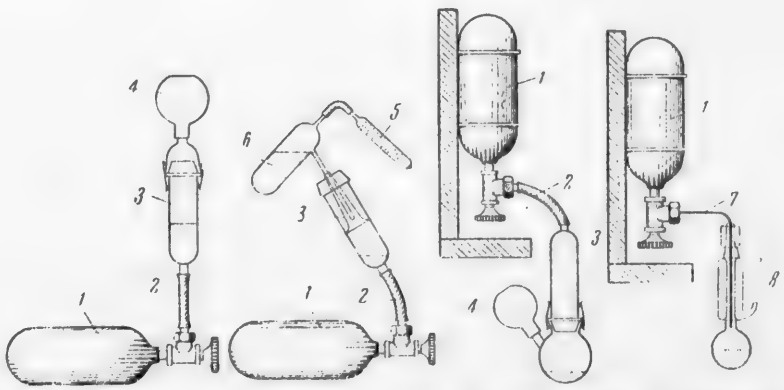

Fig. 5. 1) Reaction vessel; 2) rubber shunt; 3) glass funnel; 4) rubber bulb; 5) trap with P_2O_5; 6) ampoule with two capillary sideshoots for samples with high deuterium concentrations; 7) metal capillary; 8) receiver of the purification apparatus.

Density Determination

The density of the water is calculated from two measurements in different pyknometers. In order to

determine the density of the water, one of the pyknometers is filled with standard water, and the second with with test water. They are placed in the thermostat at the same time, and are placed on the balance pans together with the calibration weights in exactly the same way as was done during calibration. Taking into account the balance readings during calibration, the difference is determined between the weights of the test and and standard water P' in the volume of the pyknometer to be filled with test water at the thermostat temperature. The weighing results are reduced to those in vacuo: $\Delta P = \Delta P' - \delta \Delta P'/d$, where δ is the density of the air during weighing, and d is the density of the weights. All the other loads on the balance pans at the moment of determining $\Delta P'$ are not necessary for correcting for the density of the air, since they were used during the calibration. Knowing the true values of ΔP and the weight of the standard water in the volume of the pyknometer P, $\rho/\rho_0 = \Delta P/P$ is found for the test sample.

The isotopic composition of the middle fraction collected differs slightly from that of the original sample, as a result of the removal of the initial and final fractions (10% of the volume of water being distilled). Accordingly, it is necessary to apply corrections which are obtained by means of the Rayleigh formula for the distillation effect – to the results for $\Delta \rho/\rho_0$; these corrections, which are given in Table 1, are only significant at average concentrations.

Determinations of ρ_D/ρ_0 and ρ_k/ρ_0

For separate determination of the increase in density arising from the deuterium $\Delta \rho_D/\rho_0$, and the heavy isotopes of oxygen $\Delta \rho_k/\rho_0$, use is made of the phenomenon of isotopic exchange between the test water and carbon dioxide. A certain amount of carbon dioxide and the test water are introduced into the reaction vessel.* After the time necessary for establishment of isotopic equilibrium has expired, the water is poured out of the vessel.

Having determined the density of the water before the isotopic reaction and after it, and knowing the weight of water and carbon dioxide participating in the reaction, it is possible to determine the value of $\Delta \rho_k/\rho_0$ in the original water [8]:

$$\frac{\Delta \rho_k}{\rho_o} = \left(\alpha_k \frac{M_1 P}{2MP_1} + 1\right)\left(\frac{\Delta \rho}{\rho_o} - \frac{\Delta \rho'}{\rho_o}\right),$$

where $\Delta \rho/\rho_0$ is measured before the reaction; $\Delta \rho'/\rho_0$ is measured after the reaction; P is the weight of the water; P_1 is the weight of carbon dioxide; M is the mean molecular weight of water; M_1 is the mean molecular weight of carbon dioxide; a_k is the partition coefficient between water and carbon dioxide (to the first approximation, on the basis of the O^{18} isotope).

The mean molecular weight of the test water can be calculated by means of the formula

$$M = M_{H_2O} + \frac{M_{D_2O} - M_{H_2O}}{d_{25}^{25} - 1} \cdot \frac{\Delta \rho}{\rho_o} = 18{,}02 + 18{,}68 \cdot \frac{\Delta \rho}{\rho_o},$$

where M_{D_2O} and M_{H_2O} are the molecular weights of 100%, deuterium oxide and standard water respectivley, d_{25}^{25} is the ratio of their densities at 25° (the value of $\Delta \rho/\rho_0$ is taken at 25°).

At 90° for the system $H_2O - CO_2$, i.e. at low deuterium concentrations, when the exchange is determined mainly by the reaction $H_2O^{18} + CO^{16}O^{16} \rightleftharpoons H_2O^{16} + CO^{16}O^{18}$, $\alpha_k = [H_2O^{18}]\,[CO^{16}O^{16}]/[H_2O^{16}]\,[CO^{16}O^{18}] = 0.96$; for the system $D_2O - CO_2$ i.e. at high deuterium concentrations when the exchange is determined mainly by the reaction $D_2O^{18} + CO^{16}O^{16} \rightleftharpoons D_2O^{16} + CO^{16}O^{18}$, $\alpha_k = [D_2O^{18}]\,[CO^{16}O^{16}]/[D_2O^{16}]\,[CO^{16}O^{18}] = 0.98$ [9.10].

The value of $\Delta \rho_D/\rho_0$ in the original water is calculated from the measured values of $\Delta \rho/\rho_0$ and $\Delta \rho_k/\rho_0$.

The setup used for introducing the water into the reaction vessel and for subsequently pouring it out is shown schematically in Fig. 5. Before filling with test water, the filling setup and the vessels are rinsed. The sample is

*A standard 2 liter cylinder at an operating pressure of 150 atmospheres.

then introduced into the reaction vessel (about 50 or 120 ml depending on whether 10 or 25 ml pyknometers are used). The small amount of water remaining in the connecting tube outside the vessels is removed with filter paper. The connecting tube is sealed with a stopper. The vessel and sample are weighed and then filled with CO_2 gas* through a reducer, a capillary containing P_2O_5. About 300 g of CO_2 is introduced when about 50 ml of water is used, while about 600 g of CO_2 is introduced when about 120 g of water is used. The connecting tube is then sealed up again. Vessel plus water plus carbon dioxide are weighed. The isotopic exchange reaction is carried out in a water thermostat at 90°, the vessel being rotated (about half a revolution a minute). Repeated control experiments showed that at 90° the original carbon dioxide is found in isotopic equilibrium with natural water. ** Accordingly, the excess (or deficit) of the heavy isotopes of oxygen in the water, as compared with the normal isotopic composition, is distributed between the oxygen of the water and the oxygen of the CO_2, depening on the number of molecules of reactants and the partition coefficient between them. The weight of the vessel plus water and CO_2 was always the same before and after the reaction.

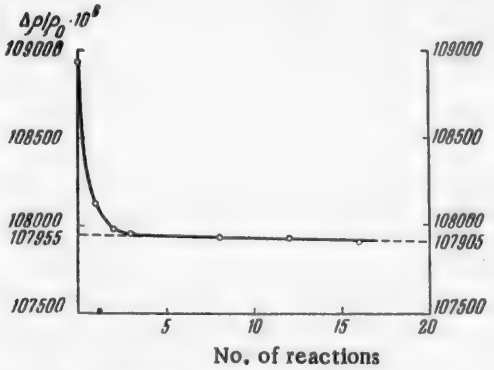

Fig. 6. Relation between the value of $\Delta\rho/\rho_0$ at 30° and the number of isotopic reactions; about 300 g of CO_2 and about 50 g of water were introduced into the vessel, C_D = 99.9%.

It is also possible to determine the value of $\Delta\rho_D/\rho_0$ directly. Known amounts of test water and CO_2 are introduced into the reaction vessel as before. After isotopic equilibrium has been established the gas is released and a new lot of CO_2 introduced into the vessel and the reaction repeated a anew. Since the original carbon dioxide will be in isotopic equilibrium with the natural water, then as a result of several reactions, the isotopic composition of the oxygen in the water will approach the normal composition. By measuring the density of the water after all the reactions, we can find $\Delta\rho_D/\rho_0$ directly. The number of "reactions" required in an actual analysis can be readily determined on the basis of the number of gram molecules of water and CO_2 (in each reaction). From the curve in Fig. 6. it is obvious that initially $\Delta\rho/\rho_0$ drops sharply, and then (after three reactions) decreases very slowly and proportionally to the number of reactions. The linear portion of the curve is determined by the dilution of the sample with natural water. On an average, during each reaction $\Delta\rho/\rho_0$ decreases by about 0.0000025, and in three reactions decreases by about 0.0000075. But, after three reactions, excess of the heavy isotopes of oxygen remains in the sample, and determines the increase of 0.000006 in $\Delta\rho_D/\rho_k$. Moreover, as a result of several reactions, the test water is brought into isotopic equilibrium with the original carbon dioxide. Bearing in mind the distribution of O^{17} and O^{18} in nature, and also the differences in the partition coefficient α_k in the systems H_2O-CO_2 it is necessary to subtract a correction of 0.000004 from $\Delta\rho/\rho_0$. Thus, the over-all correction to be applied to the measured value of $\Delta\rho_D/\rho_0$ in the example just quoted is 0.000003 after three reactions.

As an example, curves for the establishment of isotopic equilibrium in the reaction vessel are shown in Fig. 7 for the systems H_2O-CO_2 and D_2O-CO_2.

Determination of the Concentration.

The concentration of deuterium in water is calculated from the relation [8]:

$$C_D = C_D^0 + A\frac{\Delta\rho_D}{\rho_D} + B\left(\frac{\Delta\rho_0}{\rho_0}\right)^2,$$

where $\Delta\rho_D/\rho_0$ is measured; C_D^0 = 0.00015 is the concentration of deuterium in natural water; A and B are coefficients determined by the masses of the stable isotopes of hydrogen and oxygen, their distribution in nature, and by the value at a given temperature t of the ratio of the densities $d_t^t = (\rho^{100}/\rho_0)$, where ρ^{100} is the density of 100% deuterium oxide with a normal isotopic composition for oxygen. The values of coefficients

*We used liquid carbon dioxide produced from dry ice. Caron dioxide obtained as a byproduct in fermentation process cannot be used.

**The concentration of O^{17} and O^{18} is low in nature, while α_k approximates to unity and is only slightly dependent on temperature.

A and B and the values of d_t^t in the range 21-30° are given in Table 2. They are calculated on the basis of the values of $d_{25}^{25} - 1.10772$ [4] and the temperature relationship d_t^t [2].

Another, approximate method of calculation can be recommended for the determination of deuterium concentrations approximating to 100%. Assuming that over a small range the concentration of deuterium is a linear function of $\Delta\rho_D/\rho_0$ we obtain $C_D = (\Delta\rho_D/\rho_0)/d_t^t - 1)$. Small concentrations of the heavy isotopes of oxygen (up to one percent) can be determined without taking into account the square member: $C_D = C_k^0 + A(\Delta\rho_k/\rho_0)$ where $C_k^0 = 0.00219$ [2.3].

TABLE 2

t° C	d_t^t	A	B	t° C	d_t^t	A	B
21	1,10742	9,2707	0,346	26	1,10779	9,2421	0,313
22	1,10750	9,2645	0,339	27	1,10786	9,2369	0,307
23	1,10758	9,2585	0,332	28	1 10792	9,2321	0,301
24	1,10765	9,2525	0,325	29	1,10798	9,2275	0,296
25	1,10772	9,2474	0,319	30	1,10804	9,2229	0,291

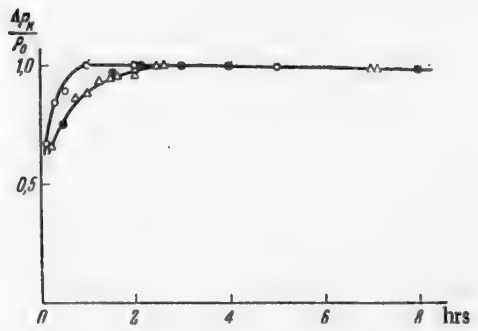

Fig. 7. Curves for the establishment of isotopic equilibrium (in relative units):
O) about 300 g of CO_2 and about 50 g of water introduced into the vessel, C_D = 1% and G_k=1%; Δ) about 300 g CO_2 and about 50 g of water introduced into the vessel, C_D = 99.7%, C_k = = 1%.

When the concentration of the heavy isotopes of oxygen is known, the volume of water used for determining the concentration of deuterium is about 50 ml when using small pyknometers (about 10 ml), and about 120 ml when using large pyknometers (about 25 ml). For determination of both concentrations, the volume of water is approximately doubled. As a rule, samples with low concentrations are analyzed in 25 ml pyknometers, while samples with high concentrations are analyzed in 10 ml pyknometers. Irrevocable losses during analysis amount to less than 20% of the original volume of sample.

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SUMMARY

A method for mass analysis has been developed which makes it possible to determine the deuterium concentration of water with an accuracy of ± 0.001% at very low concentrations, and with an accuracy of ±0.01% for very high concentrations (from about 99% and higher), as long as the concentration of the heavy isotopes of oxygen is known. Where it is necessary to measure the concentration of deuterium and that of the heavy isotopes of oxygen, the corresponding errors almost double.

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DETERMINATION OF SMALL AMOUNTS OF NITROGEN IN METALS AND ALLOYS

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Nitrogen is present in metals and alloys mainly in the form of nitrides. Determination of nitride nitrogen is usually carried out by distillation, this consists of getting the sample into solution, converting the nitrogen into ammonia, distilling the ammonia in a special apparatus, and titrating the solution obtained with acid, or the ammonia is determined photometrically.

Methods of dissolving metals and alloys are treated fairly adequately in the literature devoted to the determination of nitrogen [1-4]. For materials which are difficult to dissolve we can recommend a flask with a modified seal (Fig. 1), which prevents possible volatilization of the ammonia and too rapid evaporation of the acid used for dissolving the material. Many variants of the apparatus used for distilling the ammonia have been suggested [1-4].

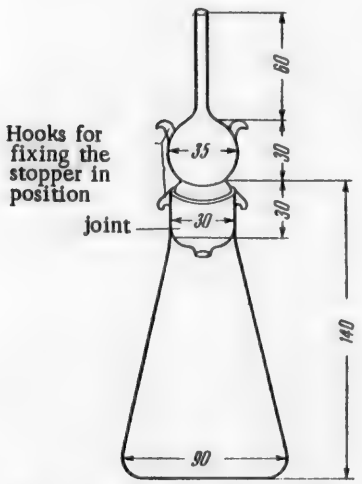

Fig. 1. Flask for decomposition of sample.

According to our experiments steam distillation is the most effective method. The somewhat modified construction of the basic part of the distillation apparatus is shown in Fig. 2. The various constructions which have been suggested for the splash head which prevents alkali from getting into the receiver, suffer from some drawback or other which is reflected in the results obtained, which can be either too high or too low. As experience has shown, the narrow tube of the splash head is usually filled with condensate, and the splashings of alkali which get into the splash head get mixed with the condensate in the tube, this liquid is then moved by the water vapor stream into the upper tubes of the apparatus, and, in this way the alkali can be partially trapped by the condensate in the receiver. The same thing happens when the condenser is placed directly over the distillation flask. In order to avoid this we suggest the use of a splash head with wide tubes (up to 10 mm) at the ends and with a widened part in the middle (Fig. 2). When the steam is sucked over slowly and uniformly, it partly condenses on the splash head walls, and washes the randomly falling splashes, and the liquid drops below without filling the tubes.

The correction in the blank experiment depends to a very large extent on the leaching out of the glass. Because of this, some parts of the apparatus (the splash head, condenser, and receiver) are made from quartz; this reduces the experimental error considerably.

For the determination of small amounts of nitrogen in metals and alloys a fairly sensitive photometric reaction is necessary. We have developed a photometric method for the determination of small amounts of nitrogen which is based on measuring the pH of the solution obtained during distillation (distillation of the ammonia), the pH is measured with the aid of a scale of matching filters and the appropriate universal indicator from the VIMS scheame used for determination of the pH of water [5]. By means of this method it is possible to

determine thousandths and ten thousandths of a percent of nitrogen in the test material. By using dilute solutions or by decreasing the weight of sample, it is possible to determine up to tenths of a percent of nitrogen.

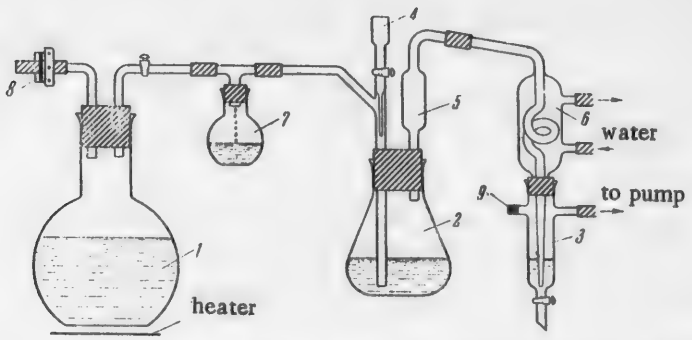

Fig. 2. Schematic diagram of the setup used for distillation of nitrogen
1) Steam generator (1-1.5 liter flask-; 2) distillation flask 300-400 ml; 3) quartz receiver; 4) funnel for introducing test solution; 5) quartz splash head; 6) quartz condenser (the long central part reaches right down into the receiver); 7) safety valve; 8) Hoffman clip for regulating the steam pressure; 9) opening for washing (under a rubber stopper).

The sensitivity of the method is 0.2 γ N in 1 ml. Photometric measurements after distillation of the ammonia does not take more than 2 minutes. The accuracy of the method is limited by the blank correction.

EXPERIMENTAL METHODS

0.1 to 3.0 g of metal or alloy is placed in the flask in which it is to be dissolved and the necessary amount of acid or mixture of acids – depending on the nature of the material to be decomposed – added. Dissolution is started in the cold, and then with heating; excess acid is best removed by evaporation. The transparent residue in the flask is diluted to 100-150 ml with distilled water.

Towards the end of the dissolution process the apparatus is prepared ready for distillation of the ammonia. The water is brought to the boil in the steam generator and steam passed through all the apparatus for 10-15 minutes, the condensate which collects in the receiver and the distillation flask being then rejected. 50 ml of NaOH (500 g/liter) is introduced into the distillation flask and steam passed through with slow suction (about 100 bubbles a minute) for 10-15 minutes, after which the vacuum is switched off, the tap of the separating funnel over the distillation flask is opened and the steam switched off. The liquid is poured out of the receiver and rejected. 5 ml of the working solution of H_2SO_4 is accurately measured into the receiver through the side tube and the latter then closed with a stopper. The test solution is then slowly poured through the funnel into the distillation flask, the flask being swirled continuously all the time. The walls of the flask and funnel are washed with the smallest possible lots of water and the tap of the funnel closed. The tap through which steam is passed into the distillation flask is opened, and the liquid in the latter agitated for some time, the vacuum is then switched on. As soon as the liquid in the distillation flask has been heated up to the boiling point, the steam passes into the splash head and the tubes leading into the condenser and heats them. From this point the distillation is carried out for 15 minutes with regular boiling and under weak suction. The ammonia liberated is taken over by the steam and dissolves in the condensate formed, and is collected in the receiver. Usually 30-40 ml of liquid are collected by the end of distillation. The vacuum is switched off and the tap of the funnel rapidly opened so as to let air into the distillation flask, the steam is then switched off. The splash head and condenser are disconnected and the distillate obtained poured into a 50 ml standard flask. The condenser and receiver are washed with twice distilled water dispensed from a special wash bottle, and the washings collected in the same standard flask. The solution in the standard flask is made up to the mark with water and the whole thoroughly mixed. Photometric measurements are then made.

For this purpose a drawing board with a scale of matching light filters is placed on a white sheet of paper while a plate with empty cells is placed on the left hand side. Into one of these empty cells is measured out exactly two drops of universal indicator, while with another pipet, test solution is withdrawn from the flask and 5 drops of it placed in the same cell. The plate is slightly shaken by tapping with the finger so that the test solution is mixed with the indicator. The color of the test solution is then compared immediately with the scale of matching colors, and the nearest match chosen. The required pH value is given against the corresponding light filter. When the color shade lies between two adjacent light filters the mean value is taken. On the basis of a table compiled beforehand, the amount of nitrogen to which the pH value found corresponds is then established (the table is compiled taking into account the total volume of solution). From the amount of nitrogen thus found the percentrate of nitrogen in the test material is then found (by multiplying by 100 and dividing by the weight of sample taken).

When the pH value is high and is outside the scale limits the test solution can be diluted appropriately with null solution. For more accurate results, another smaller sample is taken.

When the nitrogen content is very low, the aliquot is correspondingly increased.

Determination of small amounts of nitrogen should be carried out on two or three parallel aliquots, one or two blank runs being carried out as well through all the stages of the analysis, the conditions being kept strictly constant.

It is obvious of course that the reagents used for the analysis should be as pure as possible so as to cut down the blank correction.

Photometric measurements should not take more than 1-2 minutes, since on standing, the color of the test solution may change leading to higher or lower pH values as the result of the action of the air.

Experimental Conditions

No work involving nitric acid, ammonia, or ammonium salts should be carried out in the room where nitrogen determinations are carried out. The air should be neutral (no acid or alkaline vapors should be present in the air).

Vessels (flasks, beakers, wash bottles, pipets, etc) and also the apparatus used for distilling the ammonia should, before starting the analysis, be washed out carefully and steamed, and should only be used for this particular work in future.

The same wash bottle should not be used for transferring the acid solution into the distillation flask, and for washing the parts of the condenser and receiver after distilling the ammonia, since in the first instance there is a danger of sucking up acid vapors into the wash bottle which will affect the pH of the water in this bottle. The edges of the vessels should not be touched with the tip of the wash bottle during washing. The wash bottle should be operated with a rubber bulb so as not to affect the pH of the water.

The stock and working solutions of ammonia and acid, as well as the indicators (see reagents) should be prepared immediately before an analysis, and only in sufficient amount for the work in hand. Compilation of the table, carrying out the series of blank experiments, and determinati n of nitrogen in the samples, should all be carried out with the same solutions. When any reagent or indicator has to be prepared anew, it is necessary to check before everything, the table, starting with the null solution, so as to establish whether there has been any shift of the color shade with respect to the quoted values. If they are stored for some time, the indicator and solutions should be checked from time to time against the scale.

The indicator and board with the scale of matching light filters must not be left exposed to light. After comparison the board should be stowed in a container.

The pipets used for the indicator and test solution are best made from similar tubes and should have openings of the same diameter at the tip. The size of the drops should be constant; for this purpose the pipet should be held strictly perpendicular during drainage. The pipets used for compiling the table should also be used for the determination of nitrogen in samples. If the pipets are changed then the table should be checked.

It has been observed that during the transfer of very strongly acid test solutions into the distillation flask without taking any special precautions, acid vapors appear in the flask above the liquid, these vapors on being

sucked into the receiver distort the results considerably. Accordingly, acid test solutions should, if possible, be diluted, and during their transfer into the distillation flask should be introduced carefully through a funnel with a narrow internal tube (Fig. 2) the distillation flask being given a constant swirling motion during the addition.

When working with boards of VIMS matching light filters we used intervals which define the color changes more clearly. Thus, boards with pH values from 4 to 8 are only suitable for work in the range 4.5 to 7.2.

Reagents

Twice-distilled water is prepared in an all-glass distillation apparatus. The distillate is poured into a 3-4 liter distillation flask to fill the latter to two-thirds of its volume, it is then acidified with sulfuric acid and colored violet with MnO_4. Not more than two-thirds of the volume taken is distilled. The pH is measured by means of the scale of matching light filters. By maintaining standard conditions water whose pH is always the same can be obtained.

Sodium Hydroxide (500 g/liter), free from ammonia. Test for freedom from ammonia by taking 50 ml of the sodium hydroxide solution in a distillation flask and dilute with 100 ml of water free from ammonia; steam distillation is then carried out as usual for 15 minutes. Any ammonia is determined by the method indicated above by measuring the pH.

Hydrochloric or Sulfuric Acid (1:1) or other acids required for decomposing the samples should be free from ammonia. Their ammonia content is checked by diluting 25 ml of acid with 100 ml of water free from ammonia, and transferring the solution carefully through a funnel into a distillation flask containing 50 ml of sodium hydroxide which has previously been checked for its ammonia content. Distillation is carried out as usual and the ammonia content determined on the basis of the pH value.

Determination of Nitrogen in Standard Samples

Samples	Specified content of N, %	N actually found, %	Sample weight, g
Steel No. 207	0,006	0,004	5
		0,004	1
		0,004	2
		0,004	3
Steel No. 206	0,013	0,014	0,5
		0,011	0,5
		0,012	0,5
		0,013	0,5
Steel No. 159	0,11	0,107	0,1
		0,103	0,1
		0,112	0,2

Standard 0.05 N ammonia solution is prepared by diluting a concentrated solution. 3.4 ml of 14.97% NH_4OH is diluted with twice distilled water to 1 liter. The solution obtained contains approximately 0.0007 g of N per ml. The solution obtained contains approximately 0.0007 g of N per ml. The solution is standardized against 0.05 N H_2SO_4.

The working solution of 0.001 N NH_4OH which is used for compiling the Table is prepared by diluting the standard solution. 1 ml of the 0.001 N working solution contains 0.000014 g N.

H_2SO_4 Solution. A stock solution of 0.05 N H_2SO_4 is prepared first. The working solution — used for the scale with a value of 4 to 8 — is prepared by dilution. 30 ml of 0.05 N H_2SO_4 is diluted with twice distilled water to 1 liter. 5 ml of this solution on dilution to 50 ml should have a pH of about 4.5-4.7. This solution is the null solution for compiling the Table (see below). In view of the instability of the working solution it should be periodically checked.

Universal Indicator for the scale of matching light filters with pH values from 4 to 8. First solution; 0.1 of bromothymol blue is dissolved in 50 ml of ethanol, and 150 ml of twice distilled water heated to 80° added, the whole is mixed and 3 ml of 0.05 N NaOH added. Second solution: 0.05 g of methyl red is dissolved in 50 ml of ethanol and 20 ml of twice-distilled water heated to 90° added, 3.75 ml of 0.05 N NaOH is added to the hot solution. On cooling, the two solutions are mixed in the proportion of 1:1.

Table for Determination of Nitrogen on the Basis of the pH Value.

The Table is compiled by distilling various amounts of the standard ammonia solution in the range 14 to 200 γ. The null solution serves as the origin for the Table. 5 ml of the working solution of H_2SO_4 accurately measured out is always placed in the receiver and the distillation carried out for 15 minutes, the pH is measured as indicated for the analytical procedure. The table is operative over the pH range 4.5 to 7 2 (the extreme pH values on the scale of matching light filters are poorly distinguishable with respect to their colors).

On switching over to a scale with pH values ranging from 0.1 to 4.0 or from 8 to 11.8, respectively, the universal indicator is changed and another working solution of H_2SO_4 with an appropriate concentration is used, while another Table for determination of nitrogen on the basis of the pH value is compiled. The scale of matching light filters is shown in Fig. 3.

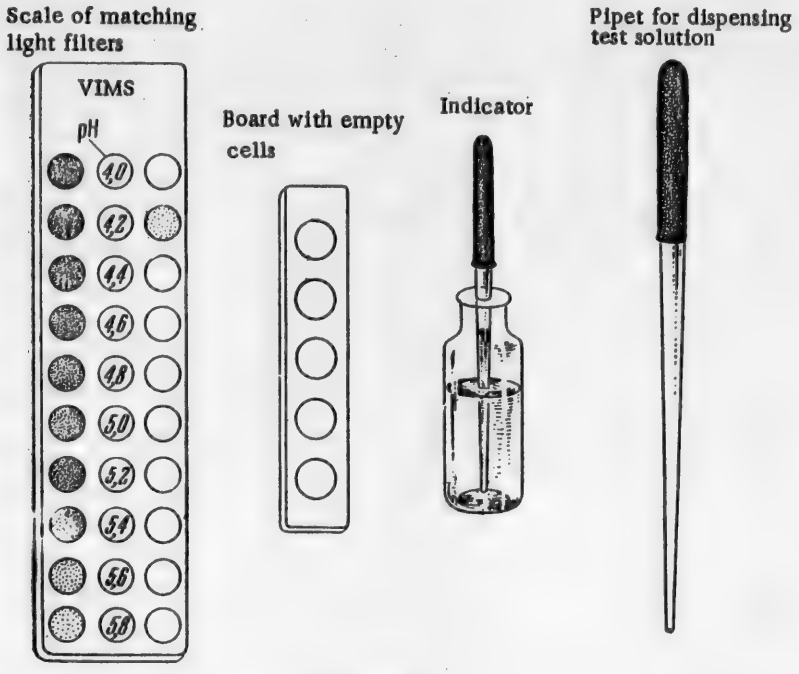

Fig. 3. Apparatus for pH determination.

SUMMARY

A new method has been developed for the determination of small amounts of nitrogen, it is based on measuring the pH of the solution obtained as a result of distillation apparatus is suggested, and a detailed description of the method is given.

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ULTRAMICROCHEMICAL STUDY OF THE COMPOSITION OF THE CELL SAP OF PLANKTON DIATOMS

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In connection with solving the problem of the buoyancy of plankton diatoms [1] the necessity arose of carrying out a chemical analysis of the cell sap of these alga. But, since the volume of the sap of even the largest of them, the so called giant tropical diatoms Ethmodiscus rex (Centrales) is only 0.5-1.5 mm^3, studies of this sap could only be carried out by means of the ultramicro method of chemical analysis [2]. Samples of the diatom Ethmodiscus were collected by K. V. Beklemishev and G. I. Semina during the voyage of the "Bityazya" in the Spring of 1955. The sap which was extracted from them by means of a piston ultramicro pipet was transferred to quartz micro vessesl with a diameter of 0.5-1.5 mm fused into glass capillaries containing a small amount of distilled water for lowering the rate of evaporation of the sap; the initial length of the column of liquid was measured under the microscope. The samples were given to us in this form for investigation.

The capillary was opened and the micro vessel removed and placed in a moist chamber on the object stage of a microscope. Twice-distilled water was added so as to bring the length of the column of liquid in the vessel to its original value, it was then centrifuged in order to mix the contents, and the volume of sap measured in a standard capillary. The sap was then returned again to the vessel and aliquots taken for determination of Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, and SO_3^{2-}. For this purpose, four moist chambers were used: one for determination of Na^+ and Mg^{2+}, another for Ca^{2+} and K^+, a third for SO_4^{2-}, and a fourth for Cl^-.

The chemical methods were chosen bearing in mind the characteristics and possibilities of ultramicro analysis. We endeavoured also to choose methods which would enable the minimum volume of sap to be used for each determination, and would make it possible to carry out parallel determinations for each of the ions in most cases.

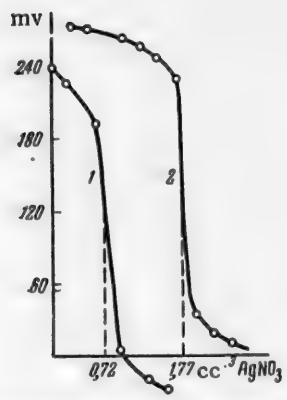
The techniques chosen were tried out beforehand on solutions (imitating sea water) taken in identical volumes, and obtained results which were in satisfactory agreement with calculated results. The Table contains results for the analysis of sea water. Descriptions are given below of the chemical techniques used for determination of each of the ions in cell sap.

Analysis of Sea Water.

Taken, μg	Found, μg	Error, %	Taken, μg	Found, μg	Error, %	Taken, μg	Found, μg	Error %
	Cl^-			Na^+			K^+	
0,330	0,327	−1	0,23	0,236	+3	0,033	0,031	−6
0,412	0,42	+2	0,24	0,244	+2	0,033	0,036	+10
	Ca^{2+}			Mg^{2+}			SO_4^{2-}	
0,0348	0,0365	+5	0,0055	0,0058	+7	0,23	0,24	+5
0,033	0,0310	−7	0,0055	0,0050	−10	0,23	0,245	+8

Determination of Chloride

For determination of chloride, in contrast ot the Mohr or Volhard methods [3] which are generally adopted for analysis of sea water, we adopted the method of potentiometric titration [4] using 0.01 N silver nitrate for titration, the latter having also been standardized potentiometrically against 0.01 N NaCl. 0.020-0.025 mm^3 was measured in a standard capillary for each determination and transferred into the titration vessel filled before hand with 1 mm^3 of 0.02 N H_2SO_4; in this way an approximately 0.01 N solution of the chloride to be titrated was obtained. The titrant was added in aliquots of about 0.2 mm^3. In all cases well defined titration curves were obtained which were in good agreement with each other in parallel determinations. Titration curves for two samples are given as an example (diagram). The technique used for potentiometric ultramicrotitration has been described previously [5].



Potentiometric determination of chloride in cell sap.

Determination of Sodium

0.025-0.030 mm^3 of sap was measured in a standard capillary and transferred into a vessel with a diameter of 2mm containing about 1 mm^3 of twice-distilled water, 5 mm^3 of a saturated solution of zinc uranyl acetate was added and the mixture allowed to stand for 3 hours. 24 hours, which is the usually recommended time of standing, proved to be unnecessarily long in the case of ultra micro determination, and was also inconvenient since it is very difficult to keep such a small volume of solution constant in the course of such a long time, and appreciable increases or decreases in the volume lead to experimental error.

The precipitate of $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ which separated out was separate by centrifuging, and was washed successively with acetic acid, and ether [6] and finally dissolved in 1.5- 2mm^3 of water, 2-3 crystals of solid $(NH_4)_2CO_3$, 0.2-0.3 mm in diameter being added by means of the sealed tip of a pipet during this process, 0.1- 0.2 mm^3 of 3 N NH_4OH was finally added. The solution was titrated with 0.1 M Complexon III solution using eriochrome black T as indicator [7] on a white background; the color change was observed with the naked eye. Here as for all titrimetric determinations, a buret with an adjusting micrometer was used [5].

Determination of Calcium

0.1 mm^3 of sap, as for the case of Na^+, was transferred to a vessel containing 1 mm^3 of twice distilled water, 0.3 mm^3 of 1 N NaOH was added and the solution titrated with 0.01 M Complexon III using murexide [7] as indicator on a white background; titration was carried out against an untitrated reference standard so as to establish the color change more accurately. Ca^{2+} was also determined in sea water and in several sap samples amperometrically, excess Ce^{4+} being titrated with Mohr's salt at E = +1 volt, after dissolving the precipitate of calcium oxalate. The results obtained when this technique was used were in good agreement with the complexonometric results. The amperometric titration technique has been described previously [8].

Determination of Magnesium

Mg^{2+} ions, in contrast to the hydroxyquinoline method [3] usually adopted for analysis of sea water, was determined by means of the reaction with titan yellow since a small content of this metal was expected. 0.005-0.1 mm^3 of the sap was transferred to a vessel containing 0.3 mm^3 of distilled water, and 0.1 mm^3 each of 5% saccharose solution and hydroxylamine hydrochloride added, followed by 0.05% titan yellow solution and 0.5 mm^3 of 1 N NaOH solution. The solution obtained was transferred to a coloriscopic capillary 0.3 mm in diameter and 10 mm long, and the color compared with a standard solution prepared in the same way.

Determination of Sulfate Ions

Sulfate ions were determined photometrically with barium chloranilate [9]. In order to remove ions which interfere with determination of the sulfate ions, a capillary column 1 mm in diameter and 5-7 mm long packed with the ion exchange resin KU-2 was used. Into this column, without touching the resin level, about 0.3 mm^3 of twice distilled water and 0.1 mm^3 of sap were introduced. This column was then placed in another capillary

tube of the same diameter, one end of which was sealed, the column with the ion exchange resin was fitted into the second capillary so that the end of the former did not touch the bottom of the latter; centrifugation was then used to drive the liquid through the resin. The second capillary was also used for collecting 0.3 mm^3 of wash water passed through the resin. Having fixed the capillary in a holder, about 0.1 mm^3 of 2% NH_4OH solution was added to the acid solution obtained, this was followed by 0.2 mm^3 0.05 M potassium hydrogen phthalate, about 1 mm^3 of ethanol and some solid barium chloranilate, the latter being added "on the tip of a pipet" (see above(. The precipitate of sulfate and excess barium chloranilate was removed by centrifugation. The colored solution was compared with a standard solution prepared in the same way, comparison being made in coloriscopic capillaries.

Determination of Potassium

When an element forms a compound which separate out in the form of a comparatively bulky, fine crystalline precipitate, the element can be determined ultramicrochemically on the basis of the volume of this precipitate with an accuracy of ±10% [10]. Essentially, the method consists of preparing, and collecting by centrifuging, precipitates from test and standard solutions under identical conditions, the precipitates being collected in the top of the corresponding vessels. The height and diameter of the base of the precipitates, which are conical in form, are measured on the micrometric scale of a microscope and their volumes calculated. Knowing the content of the test element in the precipitate obtained from the standard, its content in the precipitate obtained from the test solution can be calculated. We used this method for determining potassium as $K_2NaCo(NO_2)_6$ [11]. To 0.1 mm^3 of sap was added 0.05 mm^3 of reagent, the solution was allowed to stand for 30 minutes and then centrifuged at the same time as a precipitate obtained in the same way from a standard solution; the precipitates were carefully collected in the top of the vessels.

SUMMARY

An ultramicro method has been developed for the determination of six elements in a volume of about 0.5 mm^3. Results were obtained for a standard solution which were in satisfactory agreement with calculated data. The composition of the cell sap of Ethmodiscus diatom has been studied.

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THE SEPARATE DETERMINATION OF PEROXIDE AND SUPERPEROXIDE OXYGEN IN SUPERPEROXIDES

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Until recently, for defining the concept of "inorganic peroxide compounds", it was considered adequate to indicate the presence in their molecules of a pair of oxygen atoms, the so called "oxygen bridge." In order to establish the composition of these compounds the "active oxygen" which is liberated during the break down of the "oxygen bridge" is usually determined by a permanganometric, iodometric, or gasometric method. A. more detailed study of the structure and composition of a number of representatives of this large class of compounds has shown that some of them differ essentially with respect to the nature of the bonds between the oxygen atoms in the "bridge." In particular, it has been established that the crystal lattices of the peroxides consist of metal ions and of molecular anions of O_2^{-}, with the structure $[:\dot{\underset{\cdot\cdot}{O}}:\dot{\underset{\cdot\cdot}{O}}:]^{-2}$ [1, 2], while the crystal lattices of the superperoxides consists of metal ions and of molecular anions of O_2^{-}, with the structure $[:\dot{\underset{\cdot\cdot}{O}}-\dot{\underset{\cdot\cdot}{O}}:]$ [2, 3]. The difference in the nature of the bond between the oxygen atoms in the bridge of the peroxide and superperoxide shows up particularly clearly during hydrolysis. Peroxides hydrolyze according to the equation $Me_2O_2 + 2H_2O = 2MeOH + H_2O_2$ with formation of hydrogen peroxide which can be quantitatively titrated permanganometrically in an acid medium. Superperoxides hydrolyze according to the equation: $2\,MeO_2 + 2H_2O = 2\,MeOH + H_2O_2 + O_2$. Consequently, in superperoxides, 2/3 of the "active" oxygen which we shall call "superperoxide oxygen" is liberated in the form of O_2, while 1/3 which we shall call "peroxide oxygen" is liberated as H_2O_2. Separate determination of peroxide and superperoxide oxygen on one aliquot by decomposition of the superperoxides with water cannot be realized. The alkali thereby formed leads to decomposition of the H_2O_2 and to distortion of the analytical results. Seyb and Kleinberg [4] have developed a gasometric method for the determination of peroxide and superperoxide in NaO_2 and KO_2, their method consists of adding 5 ml of a buffer mixture-diethyl-phthalate — to about 0.2 g of sample, this is followed by 10 ml of a mixture of glacial acetic acid (8 ml) and diethyl-phthalate (2 ml). When this is done only superperoxide oxygen is liberated. In order to determine the peroxide oxygen formed in the acetic acid solution, the hydrogen peroxide is decomposed by addition of 15 ml of a mixture of 1 M HCl and 3 M $FeCl_3$, n and the volume of oxygen thereby liberated measured.

We have established that the method of Seyb and Kleinberg gives reproducible results during the analysis of the superperoxides o the alkali metals. Nevertheless, it must be emphasized that this method is only suitable when the superperoxide oxygen content of the test samples is appreciable. It is not applicable for the analysis of preparations containing superperoxides as impurities, in view of the necessity of using samples considerably greater than 0.2 g, and consequently, large valumes of reagents and large gas burets. In order to determine superperoxide and peroxide oxygen in preparations containing the superperoxides of the alkaline-earth metals as impurities, we used the technique described in [5]where dilute CH_3COOH is used instead of diethyl phthalate. Nevertheless, it was subsequently observed that peroxide oxygen can be determined by titrating with 0.1 N $KMnO_4$, the peroxide oxygen that is formed in acetic acid solution during the gasometric determination of superperoxide by the Seyb method, since the presence of diethyl phthalate in the solution being titrated does not essentially affect the results of the determination. At present, determination of superperoxide and peroxide oxygen on one aliquot (about 0.3 g) is carried out as follows. Superperoxide oxygen is determined gasometrically by Seyb's method. During this process a gas is liberated on treating an aliquot with acetic acid, analysis is also carried out

for CO_2, since the presence of carbonate as an impurity in superperoxides is unavoidable. Peroxide oxygen is determined permanganometrically by titrating an aliquot part of the acetic acid solution containing diethyl phthalate, after making the volume of the solution up to 250 ml and acidifying with H_3PO_4 (1 : 4). In the Table are given results for the determination of peroxide and superperoxide oxygen in samples of technical NaO_2, KO_2, and in peroxide preparations of calcium, strontium, and barium containing $Ca(O_2)_2$, $Sr(O_2)_2$ and $Ba(O_2)_2$ as impurities, the latter being prepared according to a method described in [6-8]. The reliability of the determination of peroxide oxygen was confirmed by a control analysis carried out on a separate aliquot.

Determination of Peroxide and Superperoxide Oxygen in Superperoxides

Test material	Peroxide oxygen on a separate aliquot, % wt.	Sample weight	Peroxide oxygen on a separate aliquot, % wt	ml/g of superperoxide oxygen *	Superperoxide oxygen, % wt	$I_{Me^{II}O_2}$, % wt.
Technical NaO_2	12,40	0,3040	12,38	184,53	26,37	90,75
Technical KO_2	10,91	0,3020	10,91	150,89	21,56	95,60
Peroxide preparation of:						$Me^{II}(O_2)_2$ Wt.%
Ca	13,87	0,3207	13,83	38,91	5,56	18,08
Sr	8,78	0,3011	8,75	18,79	2,68	12,74
Ba	7,87	0,2941	7,84	9,01	1,28	8,09

*At normal temperature and pressure.

It is clear from the table that the deviation observed during the determination of peroxide oxygen on a separate aliquot without treatment with diethyl phthalate and CH_3COOH, and on an aliquot of the acetic acid solution containing diethyl phthalate, is of the order of 0.03%.

By converting into peroxide and superperoxide, and taking into account the results of the determination of CO_2 by the Fresenius method, and the amount of free alkali, the composition of the preparations indicated can be expressed in % wt. by the following figures:

1) 90,75 Na_2O_2, 3,84, Na_2O_2, 0,70 Na_2CO_3, 4,71 NaOH (by difference)
2) 95,60 KO_2, 2,36 K_2O_2, 1,66 K_2CO_3, 0,38 KOH (by difference)
3) 18,08 $Ca(O_2)_2$, 49,96 CaO_2, 10,29 $CaCO_3$, 21,67 $Ca(OH)_2$.
4) 12.74 $Sr(O_2)_2$, 55,70 Sr_2O_2, 15,82 $SrCO_3$, 16,74 $Sr(OH)_2$.
5) 8,09 $Ba(O_2)_2$, 76,46 BaO_2, 14,11 $BaCO_3$, 1,44 $Ba(OH)_2$.

SUMMARY

It has been shown that during the analysis of preparations containing peroxide and superperoside, gasometric determination of peroxide oxygen can be successfully replaced by titrating with 0.1 N $KMnO_4$ an aliquot part of the acetic acid solution containing diethyl phthalate, formed during the gasometric determination of superperoxide oxygen.

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THE OXIDATION OF DIALKYL- AND DIARYLDITHIOPHOSPHATES BY IODINE AND THEIR TITRIMETRIC DETERMINATION

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In neutral and acid media the reaction between dialkyl- and diaryldithiophophotic acids and iodine proceeds according to the equation

$$2(RO)_2PSS^- + I_2 = (RO)_2PSS - SSP(OR)_2 + 2I^-.$$

The reaction is slightly reversible [1-2], accordingly, direct titration with iodine of solutions of the dithiophosphates must be carried out to the appearance of an intense blue color of the starch (not lilac). Satisfactory results are obtained during titration of excess iodine with thiosulfate, or during the titration of non-colored dithiophosphates in the presence of organic solvents heavier than water (CCl_4, $CHCl_3$).

Our studies have shown that readily reproducible, and very accurate results, are obtained by the oxidation of dithiophosphates with excess iodine (more accurately hypoiodide) in an alkaline medium.

For establishing the equation of the reaction between iodine and nickel diethyldithiophosphate, to a known volume of a standard solution of the latter is added 6 N NaOH and excess of a standard iodine solution. After addition of iodine the concentration of the alkali should be about 1 N. The mixture is allowed to stand for 5-10 minutes, after which it is neutralized with acid and excess iodine is titrated with thiosulfate. Completion of the oxidation of dithiophosphate by iodine can be established on the basis of the clarification of the solution with the disappearance of the disulfide originally formed.

TABLE 1

Oxidation of Nickel Diethyldithiophosphate in an Alakaline Medium

$[(C_2H_5O)_2PSS]_2Ni$ taken, mg	Amt. of I_2 used for oxidation ($N_{I_2} = 0.08878$), ml	$\frac{M_{I_2}}{M_{[(C_2H_5O)_2PSS]_2N}}$
6,7	5,6	15,87
6,7	5,7	16,15
6,7	5,7	16,15
41,3	34,8	16,03
38,5	32,45	16,02
21,9	18,44	16,02
13,4	11,3	16,02
26,8	22,7	16,01
26,8	22,7	16,01

When solid dithiophosphate is taken, care must be taken before addition of iodine to decompose the phosphate completely with alkali, since parts of it may be insulated from the action of the oxidizing agent by the metal hydroxide which is formed. In order to ensure complete breakdown of the dithiophosphates of nickel, bismuth, and some other elements, it is necessary to moisten them with a drop of CCl_4 or some other solvent, and then added the necessary amount of alkali and shake the mixture so as to transfer the dithiophosphate into the aqueous phase. The procedure outlined above is then followed.

It follows from Table 1 that 16 moles of iodine correspond to one mole of nickel diethyldithiophosphate. Similar results are obtained with pyridine diphenyldithiophosphate. After oxidation of the dithiophosphate with iodine, sulfate ions can be detected in solution. Phosphate ions are absent. This leads one to conclude that in a strongly alkaline medium iodine oxidizes dithiophosphates to sulfate. The reaction can be depicted by the equation $(RO)_2PSS^- + 16I_2 + 40OH^- = (RO)_2POO^- + 4SO_4^{2-} + 32I^- + 20H_2O$, where R is an alkyl or aryl radical.

TABLE 2

Determination of Metal Dithiophosphates in an Alkaline Medium

	Dithiophosphate, mg		Error			Dithiophosphate, mg		Error	
	Taken	Found	In mg	In %		Taken	Found	In mg	In %
$[(CH_3O)_2PSS]_2Ni$	44,3	44,3	0	0	$[(C_2H_5O)_2PSS]_2Pb$	16,85	16,95	+0,1	+0,6
$[(C_2H_5O)_2PSS]_2Ni$	41,3	41,35	+0,05	+0,1	"	48,4	48,0	—0,4	—0,8
"	38,5	38,6	+0,01	+0,3	$[(C_2H_5O)_2PSS]_3Bi$	68,2	68,3	+0,1	+0,1
"	21,9	21,9	0	0	"	13,59	13,39	—0,2	—1,5
$[(C_2H_5O)_2PSS]_2Cd$	45,6	45,6	0	0	$[(C_2H_5O)_2PSS]_3In$	71,9	72,0	+0,1	+0,1
"	69,9	70,3	+0,4	+0,6					

Oxidation of nickel diethyldithiophosphate proceeds rapidly in a strongly alkaline medium. Changes in the alkali concentration over the range 0.5-1.5 N only affects the rate of oxidation, and does not affect the amount of iodine used up. When the alkali concentration of the solution is 1 N, the time required for complete oxidation of nickel diethyldithiophosphate is 5-10 minutes. The amount of iodine used up is independent of the excess of it used. The order in which the alkali and iodine is added affects the amount of iodine used up only when excess of the latter is immediately titrated with thiosulfate (after acidification). When the solution is kept for 10 minutes prior to titration, the order in which alkali and iodine is added has no effect on the amount of iodine used.

The oxidation reaction of dithiophosphates in an alkaline medium permits determination of small amounts of these compounds with a high degree of accuracy. The method is particularly suitable in those cases when the dithiophosphate has a low melting point which excludes the possibility of drying it at 105° (the dithiophosphates of lead, bismuth, etc). The results obtained (Table 2) testify to the high accuracy of the determination.

TABLE 3

Titrimetric Determination of Cadmium

Cadmium, mg		Error	
taken	found	in mg	in %
11.24	11.21	− 0.03	− 0.3
5.62	5.65	+ 0.08	+ 0.5
0.562	0.550	− 0.012	− 2
0.562	0.562	0	0

Results for the determination of cadmium are given in Table 3. The cadmium is precipitated in a neutral or acid medium with a 1.5-2 fold excess of 0.05 N nickel diethyldithiophosphate, the precipitate and solution are allowed to stand for 5-10 minutes, after which an equal volume of water is added, if the cadmium concentration of the test solution is greater than 0.01 M, the precipitate is filtered through a No. 3 glass crucible, and washed 3-4 times with water. The precipitate is treated with alkali and excess iodine added (after addition of iodine the concentration of the alkali should be 1 N), during this stage the solution initially becomes turbid as a result of the formation of the disulfide, the solution subsequently clarifies. The clear solution is neutralized with sulfuric acid and the excess iodine titrated with thiosulfate.

Our experiments showed that ethylenediaminetetracetic acid is not oxidized by iodine in a medium of 2 N NaOH even on standing for a long time (12 hours). Nevertheless, ethylenediaminetetracetic acid is not suitable for keeping metals in solution during treatment of metal dialkyl- and diaryldithiophosphates with iodine in the presence of 2 N NaOH, since at such high alkali concentrations, the complexonates of most metals (Cd, Cu, Bi, Ni) are decomposed completely or partially with the formation of hydroxides. Only those metals which form amphoteric hydroxides (Pb, Cr) remain in solution.

SUMMARY

The oxidation of dithiophosphates by iodine in a strongly alkaline medium proceeds according to the equation:

$$(RO)_2PSS^- + 16I_2 + 40\,OH^- = (RO)_2\,POO^- + 4\,SO_4^{2-} + 32I^- + 20\,H_2O$$

and is a suitable basis for the accurate titrimetric determination of small amounts of elements in the form of their dithiophosphates.

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NEW SENSITIVE REACTIONS FOR THE DETECTION OF COPPER IONS

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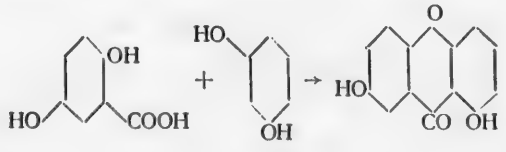
Copper ions strongly accelerate the atmospheric oxidation of an ammoniacal solution of o-aminophenol. An ammoniacal solution of o-aminophenol is colored a yellow-green color as a result of the action of air; copper ions strongly accelerate this reaction.

Detection of copper ions on the basis of the catalytic acceleration of the atmospheric oxidation of an ammoniacal solution of o-aminophenol is carried out as follows. To 1 ml of test solution is added 0.2 ml of a 1% solution of ammonia and 0.1 ml of a 0.01% aqueous solution of o-aminophenol, and the mxiture shaken. The color of the test solution and that of a control solution is observed after 1-2 minutes. When copper ions are present in the test solution, the yellow-green color appears more rapidly and is more intense than in the case of the control solution. It is possible to detect as little as 0.01 γ of Cu in 1 ml of solution at a limiting dilution of 1:100,000,000. When 0.2-0.1 γ of Cu is present in 1 ml of solution, i.e. at a limiting dilution of 1:5,000,000 - 1:100,000,000, the yellow-green color of the test solution appears during the course of one minute while in the control solution it only appears after 1 minute. At even greater dilutions the color in the test solution appears after 2-3 minutes, while in the case of the control solution the color only appears after 6-8 minutes. Silver ions also accelerate the atmospheric oxidation of an ammoniacal solution of o-aminophenol but to a lesser extent than copper. 1 γ of Ag in 1 ml of solution at a limiting dilution of 1:1,000,000 can be detected by means of its accelerating effect on the atmospheric oxidation of an ammoniacal solution of o-aminophenol.

Cation	Limit of identification, λ/ml	Limiting concentration
Cu^{2+}	0.1	1:10,000,000
Fe^{3+}	0.1	1:10,000,000
Al^{3+}	0.1	1:10,000,000
UO_2^{2+}	2.0	1:500,000
Th^{4+}	5.0	1:200,000
Ni^{2+}	20.0	1:500,000

The alkali and alkaline-earth metals as well as Mg, Be, Al, Zn, Cd, Se, Te, Fe^{3+}, Ni, Co, Pb, Mn^{2+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, Ce^{3+}, Ti^{IV}, VO_3^-, MoO_4^{2-}, WO_4^{2-}, AsO_3^{3-}, PO_4^{3-}, do not interfere with the detection of copper. Copper can be detected in the presence of elements which are precipitated by ammonia (Mn, Be, Mg, etc.) at a ratio of these elements to copper of 2000:1. In the latter instance when copper is present, the change in color occurs appreciably more rapidly in the clear layer above the precipitate than in a color test.

We have also studied the reactivity of copper ions with an alcoholic solution of euxanthone $C_{13}H_8O_4$. Euxanthone is the product obtained by the condensation of hydroquinone carboxylic acid and resorcinol on boiling with acetic anhydride:



An alcoholic solution of euxanthone forms with copper salts a yellow color the intensity of which increases with increasing copper concentration. To 1 ml of an almost neutral test solution (at a pH of 6-6-7.4) is added 0.2 ml of a 0.02% alcoholic solution of euxanthone and the whole shaken. A control test is carried out simultaneously, i.e. the reagents indicated are added in the same amounts to 1 ml of distilled water and the whole shaken; after 1-2 minutes the colors of the test and control solution are compared. When copper is present in the test solution a yellow color appears; the control solution remains colorless. 0.1 γ of Cu can be detected in 1 ml of solution by means of euxanthone.

Trivalent iron, aluminum, divalent nickel, thorium, and uranium (Table also react with euxanthone to give a yellow color.

Euxanthone permits detection of 1γ of Cu in 1 ml of solution in the presence of 1000 times its amount of Li, K, Na, Ag, NH_4^+, Rb, Mg, Sr, Ca, Zn, AsO_4^{3-}, in the presence of 100 times its amount of Pb, Ce, Te, and Ti, in the presence of 10 times its amount of Ba, and in the presence of 5 times its amount of MoO_4^{2-}

SUMMARY

A new selective catalytic reaction is described for the detection of copper ions; it is based on acceleration of the atmospheric oxidation of an ammoniacal solution of o-aminophenol, there being an appreciably more rapid change in the color of the solution when copper is present. Silver interferes.

Euxanthone $C_{13}H_8O_4$ can be used for the detection of Cu^{2+}, Al, Fe^{3+}, UO_2^{2+}, Th^{4+}, and Ni^{2+}. An alcoholic solution of the reagent reacts with the ions listed at a pH of 6.6-7.4 to give a yellow colored solution.

Received May 31, 1957.

SPECTROGRAPHIC DETERMINATION OF SMALL AMOUNTS OF HAFNIUM DIOXIDE IN ZIRCONIUM DIOXIDE

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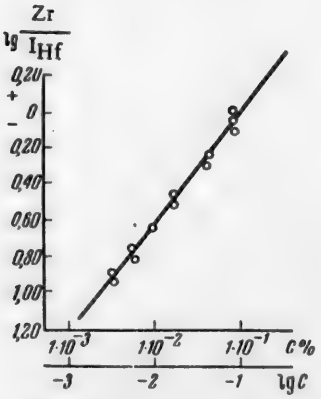
Spectrographic methods allow the determination of hundredths and tenths of a percent hafnium in zirconium [1-11]. Some authors, e.g. Mortimore and Noble [7], recommend that in order to increase the sensitivity of the determination of hafnium to 0.003%, barium fluoride be added as a buffer, and that evaporation of the samples be carried out from platform type electrodes at a high current strength (30 amps). The spectra were photographed on a grating spectrograph.

Our experiments which were carried out under the conditions suggested by Mortimore, showed that on working with a KSA-1 (KS-55) autocollimating spectrograph, addition of barium fluoride and evaporation using a high current, did not lead to an increase in the intensity of the hafnium line. Some of the increase in the intensity of the hafnium line at Hf 2641.4, when barium fluoride is added, occurs as the result of superposition of the barium line Ba 2641.37. It must be assumed therefore that the sensitivity which Mortimore achieved was mainly the result of the fact that he used a grating spectrograph with a high dispersion, which ensures a favorable relationship between the intensity of the line and that of the background.

The addition of sodium phosphate as a buffer, as recommended by Shvangiradze [8], did not give positive results either.

The requisite increase in sensitivity for the determination of hafnium when a KSA-1 (KS-55) autocollimating spectrograph with a one-lens condenser is used, was achieved by operating under the following conditions:



Calibration curve for the determination of hafnium.

20 mg of zirconium dioxide was mixed with 10 mg of carbon powder and densely packed into the opening of a rounded off graphite electrode (aode). The diameter of the rounded part was 4 mm, and the height of the rounded part was 10 mm, while the crater was 2 mm in diameter and 5 mm deep. Two electrodes filled with sample were prepared in order to get one spectrum. The upper graphite electrode was sharpened to a cone. An arc suppled with a d.c. current of 10 amps was struck between the vertically fixed electrodes. A highly magnified image of the electrodes was projected on to the slit. The central part of the flame was photographed. The slit width was 0.01 mm. Exposure time was 2 minutes. Each spectrum was obtained by superposing two spectra on the same placed on the photographic plate. (Photographic plates "Spectrographic" Type I).

The hafnium line HF 2641.4, the zirconium line Zr 2626.0, and the background near these lines were photometrically measured on the spectra obtained.

Conversion from line blackening to line intensity was carried out, taking into account the background, by using the characteristic curve of the photographic plate.

The hafnium line Hf 2641.4, the zirconium line Zr 2626.0, and the background near these lines were photometrically measured on the spectra obtained.

Conversion from line blackening to line intensity was carried out, taking into account the background, by using the characteristic curve of the photographic plate.

Determination of the hafnium concentration was carried out by means of a calibration curve constructed within the parameters:

$$\log \frac{I_{\text{Zr-background}}}{I_{\text{Hf-background}}} - \log C$$

A calibration curve for the determination of hafnium dioxide over a concentration range of 0.003 to 0.1% is shown in the diagram.

A primary standard containing 1% hafnium doxide was prepared by grinding up a mixture of zirconium oxide free from hafnium doxide with hafnium dioxide. The other standard powders were prepared by successive dilution of each of the previous standards with pure zirconium dioxide. For improving the mixing, grinding is carried out with alcohol.

The probable error of a single determination for 0.003 to 0.03% of Hf, amounts to ± 20-30%; for Hf contents greater than 0.03% this error is ± 10.0%.

The method has been used for some years for controlling the freedom of zirconium from hafnium.

We wish to thank A. K. Rusanov for his valuable advice.

SUMMARY

A spectrographic arc quantitative method has been developed for the determination of thousandths of a percent of hafnium dioxide in zirconium dioxide.

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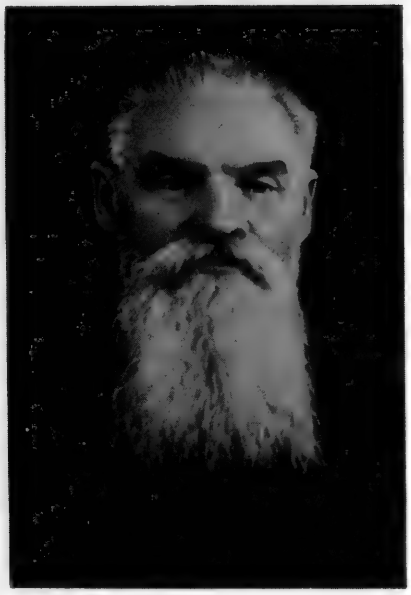


VLADIMIR IVANOVICH PETRASHEN'

(On his seventieth birthday)

On November 22, 1958 the Society of the S. Ordzhonikidze, Novocherkash Polytechnical Institute celebrated the 70th birthday, and 40 years scientific and teaching activity of one of the oldest analytical chemists, Doctor of Chemical Sciences, Professor V. I. Petrashen'.

In the course of the 40 years V. I. Petrashen' has worked as a teacher in various educational establishments of our country, and since 1928 has remained unchanged as the head of the chair of chemistry in the Novocherkask Polytechnical Institute.

V. I. Petrashen' belongs to that number of teacher-scientists who has devoted his whole life to the development of analytical chemistry.

Having started to teach analytical chemistry in 1920 in the Ural University, V. I. Petrashen' as long ago as 1922 1922, published his book"Qualitative Chemical Analysis," which, by 1948 had already reached 6 editions. This book has made the name of V. I. Petrashen' widely known in the Soviet Union and abroad. "Qualitative Chemical Analysis," has been acclaimed by famous scientists: L. V. Pisarzhevskii, I. V, Tananaev, N. N. Efremov, E. S. Przheval'skii, et al.

I. V. Tananaev wrote: Since the well known text book of N. A. Menshutkin on qualitative analysis, no text book on qualitative analysis written by a Russian author for chemistry students has existed in our literature which has proved so popular as V. I. Petrashen's book. The most distinguishing freature of this textbook is that the material within the limits of each analytical group of cations is arranged, not on the basis of the individual cations, as is done by other authors, but on the basis of the reagents used.

V. I. Petrashen's book is an original work which reflects the great scientific erudition of the author and his talent as a teacher.

The second book by V. I. Petrashen' — his textbook "Volumetric Analysis," (1946) — has also become widely known not only in Russia but abroad as well.

Under V. I. Petrashen's direction a vast amount of work has been carried out on an all-embracing study of phosphates from the point of view of their possible applications in analytical chemistry. As a result of these investigations a new method was developed for the analysis of cations of Groups II and III in the prresence of phosphate ions, as well as a systematic analytical scheme for cations which does not involve hydrogen sulfide. In addition, a number of phosphate and phosphato-colorimetric methods have been developed for the quantitative determination of manganese, lead, cadmium, bismuth, and zinc.

Petrashen' was the first to suggest a color reaction for magnesium; this reaction is now called the Petrashen' reaction.

In recent years, under the direction of V. I. Petrashen', research has been carried out on developing new methods of determining tungsten, molybdenum, mercury, chromium, aluminum, thallium, lead, etc. In the school of chemistry headed by Petrashen' new photometric methods are being developed for the determination of certain elements by means of organic reagents, while work is being carried out on the study of complex formation in solution. Petrashen' has published more than 65 scientific papers. Under his direction 24 candidate's these have been carried out and defended. Petrashen' has brought up numerous cadres of analytical chemists who work in many parts of the Soviet Union. Many of his students are leading specialists in the field of analytical chemistry. During the years of his activity, Petrashen' has prepared thousands of highly qualified specialists who are successfully working in various industries of our Socialist country.

The Commission on Analytical Chemistry, the editorial board of J. Anal. Chem. Acad. Sci. USSR, wide circles of Soviet analytical chemists, his comrades and studeents wish V. I Petrashen' long years of fruitful work for science and for the education of the young generation for the glory of our country.

CHRONICLE

THE INTERNATIONAL SYMPOSIUM ON MICROCHEMISTRY

From the 20th to the 27th of August 1958 a symposium on microchemical analysis was held in Birmingham University, England; the symposium was convened by the Midland Section, and the Group on Microchemistry of the Society of Analytical Chemistry of the International Union on Theoretical and Applied Chemistry.

About 400 delegates from 25 countries were present.

The Soviet Union delegation was represented by Corresponding Member of the Acad. Sci. USSR I. P. Alimarin, Prof. R. P. Lastovskii, A. A. Zhukhovitskii, and S. P Motorny.

The symposium was opened by an introductory address given by a member of the Royal Society, Professor Stacey of Birmingham University.

Three sections worked simultaneously at the symposium, while plenary sessions were also held in which reports by famous microchemists were read; about 50 communications by analytical chemists of various countries were given.

All the reports read can be subdivided into the following groups:

Analysis of Organic Materials

A large part of the reports dealt with modernization and development of new methods of elemental analysis (determination of carbon, hydrogen, halogens, sulfur, and also functional groups).

Radiometric Methods in Microanalysis

Worthy of attention were the following: the report by James on "Determination of Traces of Elements in Semiconductors;" the report by Bryant, Spicer, and Osmond on "Determination of Fission Products in Water and Biological Materials;" Gibbons' report on "Determination of Submicrogram Amounts of Cadmium in Superpure Zinc by Neutron-Activation Analysis."

Electrochemical Methods in Microchemistry

The following were interesting communications in this section: Kemul's report on "Separation and Determination of Traces of Organic Materials by a Chromatopolarographic Method." The wide possibilities of the application of the chromatopolarographic method for the determination of organic materials were demonstrated in this report. The author adduced some work published by him previously on this method. Calwood's report on "Polarographic Microanalysis by an Oscillographic Method." This report contained results of the very promising technique of oscillographic comparative titration. For low concentrations (10^{-5}- 10^{-9}M), preliminary electrolysis of the solution is used, after which the amalgam formed is analyzed oscillographically. The method permits determination of a large number of cations. Conditions have been worked out for the determination of certain cations in the presence of large amounts of others. The most rational electrolyte-carriers and complex forming electrolytes for various systems have been established. Ethylenediamine citrate and alkali pyrophosphate are used, after which the amalgam formed is analyzed oscillographically. The method permits determination of a large number of cations. Conditions have been worked out for the determination of certain cations in the presence of large amounts of others. The most rational electrolyte-carriers and complex forming electrolytes for various systems have been established. Ethylenediamine citrate and alkali pyrophosphate is used for the detection of Cu and Fe in cobalt salts. Tsuman's report on "The Use of Polarographic Microanalysis for the Study of Reaction Kinetics."

Professor Semerano gave a review of the possibilities of using polarography in microanalysis.

Chromatographic Microanalysis.

Only two reports were included in this section: "Chromatography of Large Molecules," and "Paper Chromatography of Inorganic Ions."

Physical Methods in Microchemistry

Four reports were given, of these mention should be made of of: "Quantitative Analysis in the Infrared," and "Flame Photometry as applied for Micro Samples and Micro Concentrations."

Organic Reagents in Chemical Analysis

This group of reports was devoted mainly to the study of complexons and metallochromic indicators (the reports of Prshibil, West, and Cheng). Prshibil's report "Research on Chelatometry in Czechoslovakia" was in the nature of a review of work carried out earlier, and partly published in journals.

West's interesting report on "New Reagents in Complexonometric Analysis" was devoted to research carried out in Birmingham University on the synthesis and study of complexons with 5-, 6-, and 7-membered rings, namely: cyclopentamethylenediaminetetracetic acid, cyclohexamethylenediaminetetracetic acid, and cycloheptamethylenediaminetetracetic acid. Of the new complexometric indicators, of interes is the indicator obtained by condensing alizarin with formaldehyde and iminodiacetic acid. The indicator can be successfully used for the determination of fluorine.

A very interesting report was that of Welcher on "Specific and Slective Reagents." This report touched upon a number of important theoretical problems in the application of organic reagents in analysis; in particular, the effect of the addendum on the stability of a complex and its capacity to be extracted by organic solvents.

Techniques of Microchemical Experiment.

This important section of microchemistry was only poorly represented at the symposium – of the 7 reports, of possible interest were the following: "The Practical Application of Chemical Microscopy" (West's report) and "Microdetermination of Physical Constants, " (Sobotka's report).

Four Lectures were delivered at the symposium. Prof. Feigl gave a lecture on "Identification of Organic Compounds by Spot Analysis." This lecture contained new, original material. The lecturer gave a number of pyrohydrolysis and hydrolysis reactions of organic compounds, as well as oxidation and reduction reactions, and catalytica reactions which permit detection of various classes of organic materials with reasonable sensitivity.

Prof. Benedetti Pichler's report was devoted to the techniques and methods of ultramicroanalysis. Of interest were new techniques of analysis by a pyrochemical method.

Prof. Lib's lecture "Organic Microanalysis," was of a review nature and contained a long historical introduction. The lecturer considered a number of methods of elemental microanalysis using various oxidizing and reducing agents. Rapid methods of determining halogens and nitrogen, and methods of determining functional groups were considered. All the methods considered were based on a gravimetric or titrimetric finish for the determination of the element or the functional group. Unfortunately, the lecturer did not touch on the question of the use of physicochemical methods such as potentiometry, polarography, etc.

Prof. Belcher's lecture was devoted to the history of the development of microchemical analysis in Birmingham University; in addition, the lecturer also discussed new research on microchemical analysis of organic compounds.

The reports which were read allowed us to get acquainted with a number of new methods of microchemical analysis of organic and inorganic materials. Microchemical methods are at present being successfully developed in many countries including the Soviet Union. The symposium gave an oppor tunity for the latest achievements in this field to be made known.

The symposium also contained an exhibition of the latest laboratory equipment, physicochemical apparatus, chemical reagents, and books as well; the exhibition was organized by English firms.

The visit of the Soviet delegation to the symposium was of great importance in establishing scientific contact with many famous analytical chemists from England and many other countries.

THE FIFTH CONFERENCE OF INDUSTRIAL AND PRODUCTION LABORATORY WORKERS OF KAZAKHSTAN AND CENTRAL ASIA

On October 14-18, 1958 ther was held at Alma Ata the Fifth Conference of the Industrial and Production Laboratory Workers of Kazakhstan and Central Asia, organized by S. M. Kirov the Kazakh State University, Acad. Sci. Kazakh SSR, by the State Scientific-Technical Committee of the Council of Ministers of the Kazakh SSR, and by the Kazakh Section of the D. I. Mendeleev All Union Chemical Society.

A large number of representatives from industrial, production, and scientific research laboratories participated in the conference; they included 150 representatives of more than 60 organizati ons of the metallurgical and chemical industries, and of laboratories of the geological service, and higher educational establishments in various towns of the Soviet Union.

The conference considered the problems confronting laboratory workers in connection with the decisions of the May Plenary Session of the central Committee of the Communist Party of the Soviet Union regarding the increased development of the chemical industry, and in connection with the program of the development of the social economy of the USSR during 1959-1965.

The conference was divided into four section: analytical, spectrographic analysis, organic technology, and the technology of mineral materials, and a total of 94 reports were read.

As a result of the exchange of opinion, on the reports that were heard, the conference adopted a resolution regarding the further development of scientific-research work in analytical chemistry and spectrographic analysis, and on questions relating to the improvement and organization of the work of factory and production laboratories. In particular, the conference recognized the basic problems of developing express and automatic methods of analysis, methods for the determination of small amounts of elements, phase analysis methods, and the develop - ment and introduction of new methods of spectrographic and flame-photometric analysis and also work on the automation of the ignition of samples and registering radiation.

A number of suggestions related to the issue of new apparatus, to increasing the issue of literature, and to the organization of courses for increasing the qualifications of workers in industrial and production laboratories, to questions of improving the training of analytical specialists within the system of the Ministry of Higher Education, and to other questions relating to the organization and improvement of the work of industrial and production laboratories.

SCIENTIFIC TECHNICAL CONFERENCE ON MODERN METHODS OF ANALYTICAL CONTROL IN BASIC CHEMICAL INDUSTRY

On 13-15 November 1958, there was held at Moscow a scientific-technical conference on modern methods of analytical control in basic chemical industry; 174 representatives from 87 enterprises, scientific-research, educational, and planning institutes took part.

On the basis of the reports which were read and on the discussions which followed the conference established that during recent years a considerable number of new chemical and physicochemical methods of analysis had been introduced into the practice of analytical control, in particular, complexonometric, and photometric,spectrographic, chromatographic, polarographic, potentiometric, mass-spectrometric, radiometric, and luminescence methods.

As a result of the discussions, the conference regarded it as essential to increase theoretical studies in order to increase the sensitivity and selectivity of chemical reactions, and also to intensify work on the search for new, sensitive reagents suitable as a basis for developing continuously operating control apparatus.

Particular attention was devoted to the necessity of developing work on the construction of new apparatus and the organization of the series production of apparatus which have proved themselves in practice.

It was decided that it is desirable to organize specialist laboratories to develop new analytical reactions and reagents for the development of rapid methods of analysis for organic and inorganic materials, and for particularly pure materials. It was suggested that the number of scientific-research laboratories based, on a number of large enterprises in basic chemical industry should be increased. The necessity was emphasized of strengthening the link between the central industrial laboratories of chemical enterprises with the scientific-research institutes and the chemistry faculties of educational establishments.

A number of resolutions adopted by the conference related to the organization of courses and seminars for improving the qualification of the workers in the central industrial laboratories, and also to the issue of sufficient textbooks on the methods of analysis for the various products of the chemical industry.

REVIEWS AND BIBLIOGRAPHY

"THE CHEMISTRY OF METAL CHELATE COMPOUNDS, by A. E. Martell and M. D. Calvin

Die Chemie der Metallchelatverbindunge, Martell A. E., Calvin M. VI, 576 pp., Verlag Chemie, G. M. B. H. Weinheim/Bergstr., 1958.

Chelate compounds are of great importance for almost all branches of chemical science. They play an outstanding role in analytical and preparative chemistry, and also in various branches of industry. A multitude of valuable, sensitive and selective methods of titrimetric, photometric, electrometric, extraction and ion exchange analysis is based on the use of chelate compounds. They enable complex problems in the separation of radioactive mixtures to be solved, and enable new, technically economic methods of controlling chemical processes to be created, processes such as water softening, flotation , emulsion polymerization, fiber dyeing, conservation of detergents, stabilization of peroxides and vitamins, purification of lubricating oil and chemical reagents, etc. Accordingly, the appearance of an American edition of the monograph under review (1952) and its German translation (1958) must be regarded as an important event in scientific chemical literature.

Results of many years work by Martell and Calvin in the field of the chemistry of chelate compounds are collected in this monograph. This was the first book in world literature in which the various published data on chelate chelate compounds were fairly completely systematized and discussed. In their book the authors have not made it their aim to give an exhaustive review of the existing literature, to give a complete survey of all known chelate compounds, or to enumerate all their applications. What they did was to endeavour to explain the general principles of the chemistry of chelate compounds, and to show by means of numerous examples the importance of these compounds for science and industry, so as to lead the reader on to search for new compounds and new applications.

Martell and Calvin's book is divided into 10 chapters.

The first chapter (16 pages) contains definitions of the basic terms, while the questions of the formation of chelate compounds are treated in a very general form, their importance is also noted.

The second chapter (52 pages) is a review of the methods used for establishing the formation of chelate compounds, and reflects the position in this field towards the end of the forties. More recent work, with few exceptions, is not considered. Chief attention is given to spectrophotometric, conductometric, potentiometric, polarographic, x-ray spectrographic, and some other methods.

In the next chapter (55 pages) the use of some of the methods listed above, as well as of some other methods, for the quantitative evaluation of the stability of chelate compounds is discussed. Such data is of great importance for calculating the various equilibria in analytical chemistry and other branches of chemistry.

The fourth and fifth chapters (63 pages) are devoted to a discussion of the significance of the structure of chelate forming materials and of metal ions for the formation of chelate compounds. Considerable attention is given to the effect of various factors on the stability of these compounds. The problem of the specificity and selectivity of analytical reagents is also touched upon.

In the 31 pages of the sixth chapter a vast amount of material relating to the nature of the chemical bond between the complex-forming ion and the donor atoms in chelate compounds is set forth. Most attention is focussed on the numberous magnetic methods which open up the greatest possibilities for determining the nature of the bond.

The seventh chapter (85 pages) is a review of the stereochemistry of chelate compounds, naturally this cannot pretend to be of exhaustive thoroughness.

The various catalytic effects of chelate compounds are discussed in the 86 pages of Chapter VIII.

The ninth and tenth chapters (73 pages) are devoted to numerous examples of the uses of chelate compound for ion exchange and extraction separation of mixtures is considered in fair detail in chapter nine.

The book finishes with a large table of stability constants for 600 chelate compounds (56 pages) with references to the original literature. The table is not up to date. The book is provided with author and subject indices; the tables and references to original work are well documented. The text includes many structural formula and diagrams. The book is printed and bound very well. The convenient arrangement of material and its clarity make it a very easy book to persue. The fairly detailed treatment of the most important question in this field make this book a valuable reference book for scientific-research, analytical, and industrial laboratories.

Since its first appearance in an American edition in 1952, this book has been widely acknowledged. The edition of a German translation will ensure that it will become even more widely known.

We can only regret that the German edition is an exact reproduction of the American original. The book would undoubtedly benefit if its translation into German had been accompanied by the inclusion of research work in the chemistry of chelate compounds published during 1951-1958, including that by Martell and Calvin, even if it were only the most important work during that period that room could be found for. During this period interesting work has been carried out on the connection between the structure of a reagent and its analytical properties, and important theoretical research has been published which opens up methods for forecasting the conditions for carrying out analytical determinations, while methods for determining the composition and evaluating the stability of chelate compounds have been develped further. In addition, a large amount of work has been carried out on the study of the composition and properties of many chelate compounds. During this period also, new methods for establishing the equivalence point have been developed (heterometric, haigh-frequency) which enhance the analytical value of chelate compounds. The number of analytical applications of these compounds for masking, for varying the oxidation-reduction potential and, for extraction and ion exchange separation of mixtures, has increased considerably. These achievements should be included in a new edition.

All the same, even in its present form, Martell and Calvin's book is of great scientific value for a wide circle of analytical chemists. The book satisfies the primary needs of research workers on the chelate compounds of metals. An enlarged Russian edition of Martell and Calvin's monograph will undoubtedly be greeted with great interest by Soviet chemists.

A. I. Busev and N. G. Polyanskii

A NEW REAGENT FOR SCANDIUM

A new reagent for the photometric determination of scandium — "Sul'fonazo" — has been synthesized at the All-Union Scientific Research Institute of Chemical Reagents (IREA).

This reagent is more selective than alizarin S, quinalizarin, and arsenazo while being approximately equal to them in sensitivity. Scandium can be determined in the presence of considerable amounts of yttrium and the rare-earths. Satisfactory results are obtained during the determination of scandium in silicate rocks, and coal-ash. The reagent possesses advantages over other reagents.

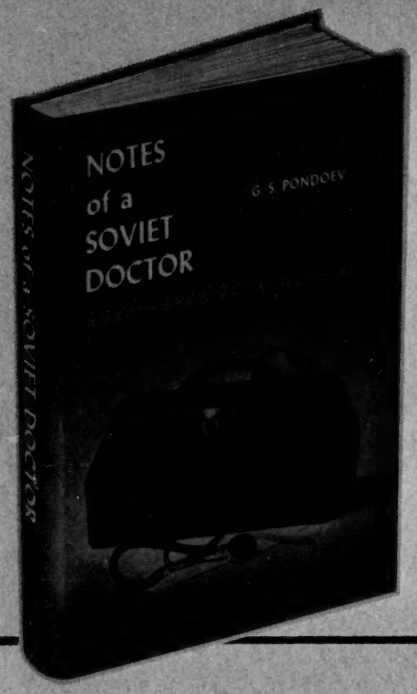
Organizations and enterprises wishing to test the new reagent can get a free sample of it, together with instructions for its use, on applying to the following address: Moscow Zh-33, Samokatnaya Ul., D-4-a-Institute of Chemical Reagents.

Sul'fonazo is not at the moment being produced on a factory scale, and in order to establish whether it is worth organizing its production, the Institute of Chemical Reagents urgently requests all those organizations and enterprises who receive samples of the new reagent to let the Institute know about the practical value of the reagent within a two-month period.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET CHEMICAL LITERATURE

Abbreviation (Transliterated)	Significance
FIAN	Phys. Inst. Acad. Sci. USSR
GIPKh	State Institute of Applied Chemistry
GIREDMET	State Rare Metals Scientific Research Institute
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GLAVKhIM	Main Administration of the Chemical Industry
GOI	State Optical Institute
GONTI	State United Sci.-Tech. Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
Gostoptekhizdat	State Scientific and Technical Publishing house of the Petroleum and Mineral Fuel Industry
GTTI	State Tech. and Theor. Lit. Press
IFKhA	Institute of Physicochemical Analysis
IL	Foreign Lit. Press
IOKhAN	Institute of Organic Chemistry of the Academy of Sciences of the USSR
IONKh	Institute of General and Inorganic Chemistry (N. S. Kurnakov)
IONKhAN	Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR
INBI	Institute of Biochemistry
IREA	Institute of Chemical Reagents
ISN (Izd. Sov. Nauk)	Soviet Science Press
IVKhTI	Ivanovo Chemical Engineering Institute
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
KEIN	Colloid Electrochemical Institute
Khimizdat	Chemistry Press
LGU	Leningrad State University
LIM	Leningrad Institute of Metals
Metallurgizdat	Metallurgy Press
MITKhT	Moscow Institute of Fine Chemical Technology
OIYaI	Joint Institute of Nuclear Studies
OKhN	Division of Chemical Science
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Division of Technical Science
RIAN	Radium Institute, Academy of Sciences of the USSR
RZhKhim	Chemical Abstract Journal (USSR)
VKhO	All-Union Chemical Society (Mendeleev)
ZhFKh	Journal of Physical Chemistry (USSR)
ZhRKhO	Journal of the Russian Chemical Society

Note: Abbreviations not on this list and not explained in the translation have been transliterated no further information about their significance being available to us. — Publisher.



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